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PREPARATION AND EXTRACTION OF S^{35} ¹

By M. B. WILK

Abstract

Procedures are described for the preparation and extraction of carrier-free S^{35} , based on the $Cl^{35}(n, p)S^{35}$ reaction. Potassium chloride, sodium chloride, and ferric chloride have been used as target materials. The S^{35} is found to appear in a chemical form which exchanges rapidly with sulphate ion. Separation of S^{35} from irradiated potassium or sodium chloride is effected by taking advantage of the insolubility of these salts in aqueous hydrochloric acid solutions. Approximately 99.8% of the salt can be removed while leaving 95% of the S^{35} in solution. Separation from irradiated ferric chloride is effected by solvent extraction of the ferric chloride from aqueous 6 to 8 M hydrochloric acid solutions. Less than 0.1% of the total solids is left unextracted. The yield of S^{35} approaches 100%.

Introduction

Isotopes of Sulphur

The isotopic composition of natural sulphur is S^{32} —95.04%, S^{33} —0.74%, S^{34} —4.2%, S^{36} —0.016%. Three radioactive sulphur isotopes have been artificially prepared. S^{31} is a positron emitter of 3.2 sec. half life. S^{35} and S^{37} decay by β^- emission with half lives of 87.1 days and 5.04 sec. respectively (10).

It is apparent, therefore, that only S^{35} bears consideration for use as a radioactive tracer.

Properties of S^{35}

The existence of a long-lived radioisotope of sulphur was first observed by Andersen (1) on neutron irradiation of carbon tetrachloride. The mass assignment of S^{35} was made by Kamen (5) on the basis of cross section considerations. Kamen (5) reports a half life of 88 days, in good agreement with the value of 87.1 days published by Hendricks *et al* (3). No appreciable gamma activity has been found in the decay of S^{35} .

The β -ray spectrum of S^{35} was studied by Libby and Lee (8), who found a maximum energy of 107 ± 20 kev. Later work by Kamen (5) gave a value of 120 ± 15 kev. More recent values differ considerably from these. Solomon, Gould, and Anfinson (12) report a value of 167 ± 4 kev., closely corresponding to values obtained by the author. Overman (9), with a value of 170 kev. and Yaffe and Justus (16), with a value of 167 kev., confirm the higher value for maximum energy of β 's from S^{35} .

¹ Manuscript received January 4, 1949.

Contribution from the Chemistry Branch, Research Division of the Atomic Energy Project, the National Research Council of Canada, Chalk River, Ontario, Canada. Issued as N.R.C. No. 1941. The paper was given at the Halifax Conference of the Chemical Institute of Canada on June 1, 1949.

Preparation of S^{35} by Means of a Chain-reacting Pile

Kamen (6) gives a summary of all known reactions which can be used to make S^{35} . While much of the early work with S^{35} was done with cyclotron-produced material, the primary source of the radioisotope at present is a chain-reacting pile. Only reactions using neutrons as the bombarding particle are discussed here.

On irradiation of sulphur with neutrons, S^{35} is formed by the reaction $S^{34}(n, \gamma)S^{35}$. This reaction occurs with thermal neutrons. The specific reaction cross section* is 0.26 barn† (2). However, the low abundance of S^{34} in natural sulphur reduces the natural atom cross section for formation of S^{35} to 0.011 barn.

Thus, even with irradiation to equilibrium at a flux of 5×10^{12} neutrons per cm^2 per sec. (available in the N.R.X. pile) the maximum specific activity obtainable would be 0.028 millicuries (mc.) per mgm. In addition, contamination with radioactive P^{32} (1.7 Mev. β , 14.7 days half life), formed by $S^{32}(n, p)P^{32}$, occurs.

A more satisfactory method for preparing S^{35} is by the transmutation reaction $Cl^{35}(n, p)S^{35}$. This reaction occurs with thermal as well as fast neutrons (5). The specific reaction cross section for the thermal neutron reaction is given as 0.169 barn (2). Since the abundance of Cl^{35} in natural chlorine is 75.4% this means a natural atom cross section of 0.13 barn. Yields obtained in the N.R.X. pile were 10 to 20 times higher than this value would indicate. The discrepancy may be due to a resonance peak in the fast neutron range.

The thermal neutron capture cross section of chlorine is about 35 barns (11). The reactions which occur on pile irradiation of chlorine are shown in Table I.

TABLE I
REACTIONS OCCURRING ON NEUTRON IRRADIATION OF CHLORINE

Isotope	Reaction	Product	Half life	Energy, Mev.		Type neutron
				β	γ	
Cl^{35}	n, γ	Cl^{36}	1×10^4 yr.	0.66	None	Thermal
Cl^{35}	n, p	S^{35}	87.1 days	0.17	None	Thermal and fast
Cl^{35}	n, α	P^{32}	14.7 days	1.7	None	Fast
Cl^{37}	n, γ	Cl^{38}	37 min.	1.1, 2.8, 5.0	1.65, 2.15	Thermal

Because of its long half life, the Cl^{36} radioactivity developed is negligible if relatively short irradiation periods are used. Short-lived Cl^{38} decays in a day or so. Contamination by P^{32} is of the order of 1% of the total S^{35} , in terms of β particles emitted. The $P^{32} : S^{35}$ ratio can be reduced by (a) long

* Specific reaction cross section = cross section for neutron capture of natural sulphur \times isotopic abundance ratio of S^{34} .

† One barn = 10^{-28} cm^2 .

term irradiations, (b) irradiation in a thermal neutron flux, and (c) a long decay period.

The selection of an appropriate target material for production of S^{35} is governed by the following criteria: stability to heat and radiation, large proportion of chlorine, minimum interference by cation activity, ease of handling and extraction, chemical purity of material, and low neutron capture cross section of cation.

Early workers (1, 5) with S^{35} used carbon tetrachloride as a target material. While carbon tetrachloride offers the attractiveness of containing 92.2% chlorine, no interfering cation activity, and low neutron capture cross section of carbon, its instability to heat and radiation seriously limits its utility. More satisfactory targets are potassium, sodium, or ferric chlorides.

Experimental Work and Discussion

MEASUREMENT OF RADIATION FROM S^{35}

The very low energy of the β particles from S^{35} poses special problems as regards their quantitative detection. Fig. 1 shows a semilogarithmic plot of a typical external absorption curve obtained with a sample of substantially carrier-free S^{35} . This curve was obtained with a sample mounted on a very thin formvar film.* If the sample is mounted on a glass tray, the shape of the absorption curve obtained will differ somewhat, owing to differences in counting geometry and to the effect of backscattering.†

The bend in the absorption curve, together with the variation in the slope of the curve with counting geometry and backscattering effects, makes it difficult to characterize the S^{35} radiation by one external absorption half-thickness for the entire range.‡ For the particular case of a sample mounted on a thin film, using the initial portion of a linear plot (see Fig. 2), 4 mgm. per $cm.^2$ will cause a 50% decrease in counting rate.

The low energy of the radiation makes self-weakening a major problem. Experiments showed that samples of thickness 3 mgm. per $cm.^2$ will be weakened to the extent of 40% of the total activity. Internal gas counters can be employed to avoid this handicap, but for routine use they are difficult to operate and are time consuming.

Yankwich *et al.* (17) and Libby (7) discuss general methods for correction of self-absorption by samples of varying thicknesses of weak β -emitters. Hendricks *et al.* (3) give data on the self-weakening of S^{35} in barium sulphate. Henriques *et al.* (4) give an analytical procedure for S^{35} based on oxidation to sulphate ion by the Carius method and subsequent precipitation as benzidine sulphate. Unfortunately, the correction factors derived from this work are

* Less than 100 $\mu gm.$ per $cm.^2$

† L. Yaffe and K. Justus at these laboratories have obtained some interesting information on backscattering of β -radiation which is to be published shortly in the *Canadian Journal of Research*.

‡ See L. E. Glendenin, *Nucleonics*, Jan. 1948, for further discussion of this point.

not based on the most recent values of the maximum energy of the S^{35} radiation, and cannot be readily applied to different counting arrangements.

In the work reported here, an "end-on" Geiger counter, having a 3.2 mgm. per cm^2 mica window, was used. The counter was mounted on a lucite

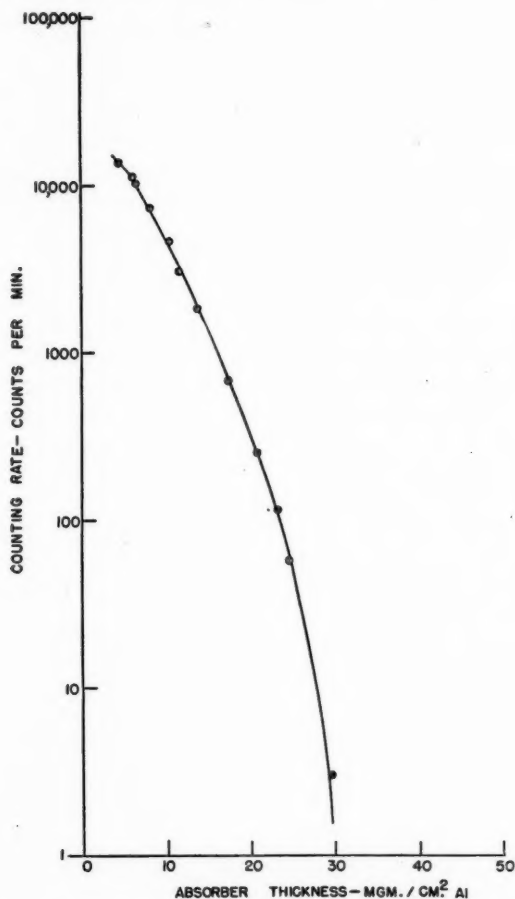


FIG. 1. Absorption measurements on S^{35} radiation (thin film mounting).

holder, and the air gap between counter and sample was held constant at 1.25 cm. Samples to be counted were deposited on watch glasses, 1 in. in diameter.

The self-weakening problem was handled as follows. All samples to be analyzed for S^{35} were made up to volume and aliquots of 0.1, 0.2, 0.3, 0.4 ml. were pipetted on to the watch glasses, evaporated to dryness, and counted.

The activities obtained were recalculated on a common volume basis, and the activity per unit volume plotted against the volume of the sample used. The curve was then extrapolated to zero volume (i.e., zero thickness of sample). It is evident that the curve must flatten as the volume approaches zero.

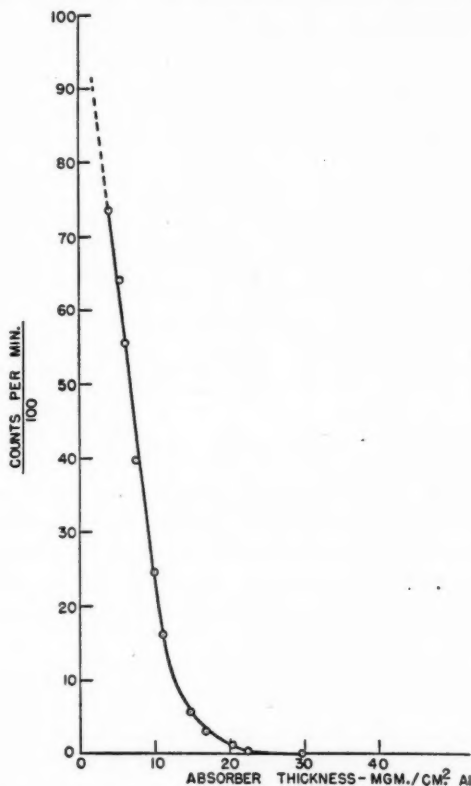


FIG. 2. Linear plot of external absorption (thin film mounting).

The activity reading at zero volume was taken as the "true" activity. This technique also served to minimize pipetting errors and check on possible evaporation losses.

EXTRACTION OF S^{35}

(a) Carbon Tetrachloride as the Target

Carbon tetrachloride was irradiated at very low neutron fluxes in an aluminum container. Considerable corrosion of the aluminum was found to occur over an irradiation period of one month.

In extracting the S^{35} , the procedure described by Kamen (5) was used as a guide. The irradiated carbon tetrachloride was refluxed with an aqueous

hydrogen peroxide solution containing some inactive sulphur and phosphorus carrier as ammonium sulphate and ammonium phosphate. The aqueous extract was separated, made basic, and magnesium ammonium phosphate precipitated. The filtrate was then made acid and barium chloride added to precipitate barium sulphate. Transfer of the precipitate was effected by slurrying with ethyl alcohol. Activity yields obtained were of the order of $60 \pm 25\%$.

(b) *Potassium or Sodium Chloride as the Target*

Table II summarizes the relevant data as regards neutron irradiation of potassium and sodium.

TABLE II
REACTIONS OCCURRING ON NEUTRON IRRADIATION OF POTASSIUM AND SODIUM

Isotope	% abundance	Reaction	Product	Cross section, barns	Half life	Energy, Mev.		Remarks
						β	γ	
K ³⁹	93.38	n, γ	K ⁴⁰	?	1×10^8 yr.	1.0	2.0	K ⁴⁰ exists in nature
K ⁴¹	6.61	n, γ	K ⁴²	0.067	12.4 hr.	3.5	None	
Na ²³	100	n, γ	Na ²⁴	0.63	14.8 hr.	1.4	1.4	
						2.8		

The long half life of K⁴⁰ makes radioactivity from it negligible. The radiation from K⁴² and Na²⁴ would be troublesome unless a decay period of about one week is allowed. Storage and handling of irradiated sodium are somewhat more complicated than for potassium because of γ -ray emission from the former. The proportion of chlorine in potassium chloride is 47.56%, in sodium chloride is 60.7%.

(i) *Separation of S³⁵ from Irradiated Potassium or Sodium Chloride with Carrier*

A satisfactory procedure for separation of S³⁵ from the irradiated alkali chloride, using inactive carrier sulphur, involves the precipitation of barium sulphate.

The irradiated salt was dissolved in water and carrier ammonium sulphate and ammonium phosphate were added. Magnesium ammonium phosphate and barium sulphate were separated as described above.

Experiments were carried out to check on the following: (a) the need to oxidize the original solution, (b) coprecipitation of S³⁵ with magnesium ammonium phosphate when no carrier sulphate is added, and (c) coprecipitation of P³² with barium sulphate when no carrier phosphate is added.

Two equal aliquots of stock solutions of irradiated alkali chloride were treated as follows: carrier sulphate and phosphate were added, and one of the aliquots was oxidized with hydrogen peroxide, the excess peroxide being destroyed by heating in hot water. Both solutions were acidified with hydrochloric acid, barium sulphate precipitated from the hot solution, and

the precipitate digested for two to three hours. Table III gives the percentage of S^{35} activity left in the filtrate after precipitation. The activity due to P^{32} was eliminated by means of absorption measurements.

TABLE III
SEPARATION OF S^{35} USING CARRIER

Target material	Treatment	S^{35} left in filtrate, %
NaCl	Oxidized	0.5
NaCl	Nonoxidized	0.8
KCl	Oxidized	0.4
KCl	Nonoxidized	1.1

It will be seen that the percentage of S^{35} left in solution after precipitation of barium sulphate is slightly higher for the nonoxidized solutions. The actual values, however, are so small that it can safely be said that the chemical form of S^{35} in neutron irradiated potassium or sodium chloride is such that it will undergo rapid exchange with sulphate ion upon solution of the target material.

Voge and Libby (14) and Voge (13) found that exchange between sulphide and sulphate, and sulphite and sulphate, was not appreciable during 36 hr. at 100° C. It seems likely, therefore, that the radioactive sulphur appears as $S^{35}O_4^{2-}$ on water dissolution of irradiated potassium or sodium chlorides.

S^{35} does not coprecipitate appreciably with magnesium ammonium phosphate even if no carrier sulphate is added, if the solution and precipitate is digested in boiling water for a few hours. If barium sulphate is precipitated from hot acid solution, and digested for a few hours in boiling water, the contamination from P^{32} coprecipitation is negligible.

(ii) *Separation of S^{35} from Irradiated Potassium or Sodium Chloride Without Carrier*

In the extraction procedures described above, the S^{35} is considerably "diluted" with inactive sulphur. The limiting factors in the specific activity obtainable are: (a) the available neutron flux and (b) the quantity of carrier which must be added concomitant with the volume of solution needed to dissolve all the potassium or sodium chloride target material.

An increase in specific activity will be effected by the removal of the excess target material. Overman (9) mentions the use of ion-exchange resins for this purpose. Preliminary experiments performed by the writer using Dowex-50 as the ion-exchange resin were discouraging. Over 50% of the S^{35} was found to adsorb on the resin in a $\frac{1}{2}$ in. diameter column, 6 in. long. An alternative technique was therefore developed, based on the insolubility of potassium and sodium chlorides in concentrated hydrochloric acid.

Following preliminary beaker experiments to test the feasibility of the process, an apparatus (Fig. 3) was constructed which could be operated with

minimum direct handling of active materials. The apparatus is operated as follows. A stream of air is passed through the sintered glass disk (*B*) after having passed through a calcium chloride drying tube (*O*). The pressure

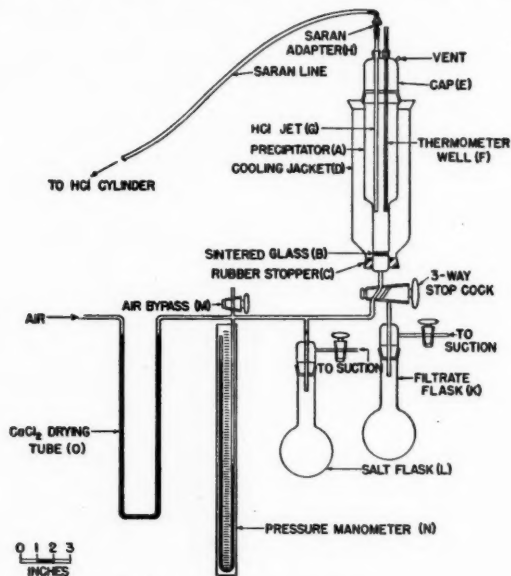


FIG. 3. S^{35} extraction apparatus.

manometer (*N*) is adjusted by control of a by-pass (*M*). A saturated solution (at room temperature) of the irradiated salt is poured into the precipitator (*A*), and is kept from running through the sintered glass by the air stream. The cap (*E*) is then put on, and hydrogen chloride gas (from a cylinder) is passed in through the jet (*G*). Cooling media (brine solution cooled by dry ice) is circulated through the cooling jacket (*D*). Since hydrogen chloride has a large heat of solution, the temperature can be used as a measure of the saturation of the solution. When the temperature of the solution falls to the desired value (-10 to -20°C.), the three-way stopcock (*J*) is turned and the filtrate drawn off by suction into a flask (*K*). The hydrogen chloride gas stream is then shut off, and the cap removed. Spray is washed from the sides of the vessel with a little concentrated hydrochloric acid.

This filtrate can then be evaporated to a small volume, concomitant with its reduced salt content, and the process repeated. The residual salt is dissolved in distilled water and drawn off after each precipitation (into flask *L*).

Two 25 gm. batches of irradiated potassium chloride (each dissolved in 100 ml. of water) were extracted in series. Their filtrates were evaporated together until a precipitate of potassium chloride appeared. Sufficient water for solution was added and a second extraction procedure carried out.

Similarly, 11 gm. of irradiated sodium chloride was put through a single precipitation procedure. Table IV lists the results obtained.

TABLE IV
SEPARATION OF S^{35} FROM IRRADIATED POTASSIUM AND SODIUM CHLORIDES

Target material	KCl	NaCl
Total weight of salt used, gm.	50	11
No. of precipitations	2	1
% Reduction in solids	99.8	99.8
% Yield of S^{35}		
In filtrate	85.5	81.0
In HCl washing	9.1	17.4
	94.6	98.4
% Lost in evaporation	1	—

The very high yields of S^{35} obtained by this process, from both potassium and sodium chlorides, together with the fact that a considerable quantity of activity is carried off by a very small volume of concentrated hydrochloric acid, would indicate that such losses as occur are due to simple wetting and not crystal occlusion. The difference in yield between sodium and potassium chlorides is not to be taken too seriously in view of the large difference in bulk of material extracted and the inaccuracies in counting S^{35} .

It is noteworthy that the solubility of sodium chloride in hydrochloric acid solutions is markedly lower than that of potassium chloride—one precipitation of sodium chloride yielding the same percentage reduction in solids as two potassium chloride precipitations.

As a possible adjunct to the procedure described above, some experiments were done on the precipitation of potassium chloride from a saturated hot solution, advantage being taken of the large temperature coefficient of solubility of potassium chloride in water. Irradiated potassium chloride was dissolved to saturation in distilled water at 70° C., cooled overnight to 10° C., filtered, and the precipitate washed with a small volume of water. It was found that about 25% of the activity remains in the precipitate. It is difficult to reconcile the different behavior, as regards contamination with S^{35} , of these two precipitation procedures.

The capacity of the apparatus shown is about 100 ml. as an upper and 5 ml. as a lower limit. If desired, the apparatus could be scaled up to accommodate much larger volumes. The lower volume limit for an apparatus of this type, below which spray losses would be excessive, is probably 1 ml.

Assuming an irradiation period of one S^{35} half life (87.1 days), a flux of 5×10^{12} neutrons per cm.² per sec., and cross section of 0.13 barn, the potential activity to solids ratio, assuming one precipitation step, would be 2 mc. per mgm. solids for potassium chloride and 3.5 mc. per mgm. solids for

sodium chloride. In fact, the effective cross section for the reaction is much larger than that used here, and hence the ratio of S^{35} to total solids would be much higher.

P^{32} formed by $Cl^{35} (n, \alpha) P^{32}$ remains with the S^{35} as a radioactive contaminant. The chemical form of the carrier-free S^{35} obtained by this process is presumably a solution of $Na_2S^{35}O_4$ or $K_2S^{35}O_4$ in hydrochloric acid. If the S^{35} is required in other chemical forms, it is likely that some inactive carrier would have to be added and normal chemical conversions carried out.

(c) *Ferric Chloride as Target*

Natural iron consists of Fe^{54} —6.04%, Fe^{56} —91.57%, Fe^{57} —2.11%, Fe^{58} —0.28%. On neutron irradiation, two reactions lead to radioactive isotopes: $Fe^{54} (n, \gamma) Fe^{55}$, $Fe^{58} (n, \gamma) Fe^{59}$. Fe^{55} decays by K capture, emitting a very soft X-ray, with a half life of about four years. Fe^{59} emits 0.26 and 0.46 Mev. β 's and 1.1 and 1.3 Mev. γ 's decaying with a 47 day half life. The total atom cross section for Fe^{59} formation is 0.001 barn.

It will be seen therefore that the interfering activity, in using ferric chloride as a target for making S^{35} , will be existent but slight. Ferric chloride consists of 34.45% iron and 65.55% chlorine.

(i) *Separation of S^{35} from Irradiated Ferric Chloride with Carrier*

Anhydrous, sublimed ferric chloride was irradiated with neutrons and a two day decay period allowed.* Experiments were carried out to determine (a) the chemical form of the S^{35} and (b) the coprecipitation of S^{35} with hydrated ferric oxide.

After solution of the irradiated ferric chloride, carrier sulphate and phosphate were added. Three aliquots were taken and to two of these a few drops of 30% hydrogen peroxide was added and the solutions heated to destroy excess peroxide. Barium sulphate was precipitated from both oxidized and unoxidized solutions, following the procedure described earlier.

Essentially no difference was found as a result of the oxidation step. The precipitation of barium sulphate leaves about 1% of the S^{35} in solution whether the solution is initially oxidized or not. It would appear, therefore, that on solution of irradiated ferric chloride, the S^{35} is present as $S^{35}O_4^{2-}$, or in a form which exchanges rapidly with sulphate ion.

Hydrated ferric oxide was precipitated from the third aliquot by addition of concentrated ammonium hydroxide. About 50% of the S^{35} and practically 100% of the P^{32} is carried down in this precipitation. As a separation method, therefore, the precipitation of hydrated ferric oxide offers little advantage.

(ii) *Separation of S^{35} from Irradiated Ferric Chloride Without Carrier*

It is well known that ferric chloride can be readily solvent-extracted from aqueous hydrochloric acid solutions with diethyl or diisopropyl ether as well as other higher ethers. The real interest in using ferric chloride as a target

* Irradiation containers used were made of (a) aluminum and (b) bakelite. Both were satisfactory from a corrosion standpoint.

material lay in the likelihood of a very efficient and simple S^{35} extraction procedure based on the solvent extraction of ferric chloride.

In the experiments reported here, isopropyl ether was used as solvent. The partition coefficient for extraction of ferric chloride by isopropyl ether from aqueous 6 M hydrochloric acid varies from 1 to 100 (15), depending on the iron concentration. For higher acidities up to 8 M hydrochloric acid the coefficient is even higher.

One gram of pile-irradiated ferric chloride was dissolved in concentrated hydrochloric acid and a few drops of 30% hydrogen peroxide added, to ensure that all the iron was present as ferric ion. (Ferrous chloride does not solvent-extract.) The solution was then diluted with distilled water to approximately 6 N in hydrochloric acid.

The aqueous solution was shaken with successive $\frac{1}{4}$ volumes of isopropyl ether until the color of ferric chloride had disappeared completely. It was then extracted twice more with $\frac{1}{4}$ volumes, and finally washed with an equal

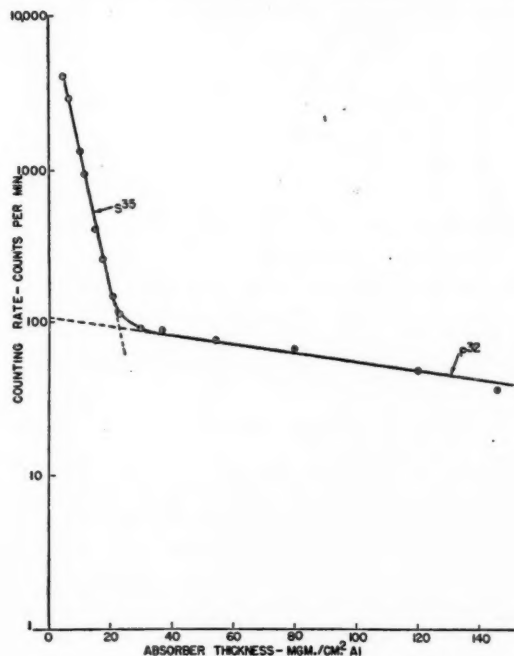


FIG. 4. Activity in aqueous residue solution.

volume of solvent. (The total volume of ether used depends on the initial concentration of ferric chloride and hydrochloric acid, as well as on the patience of the experimenter in shaking each batch for a sufficiently long period of time to ensure equilibrium.)

The ether extracts were then collectively stripped with distilled water.

The radioactivity of the resultant solutions was measured, components being differentiated by absorption measurements. An aliquot of the aqueous residue solution was evaporated to dryness to measure the total solids left.

Figs. 4, 5, and 6 give the absorption curves for the aqueous residue solution, the stripped ether, and the water extract respectively. It is evident that no detectable amount of radioactive iron remains in the aqueous residue. On the other hand, the radioactivity of S^{35} cannot be detected in the extract.

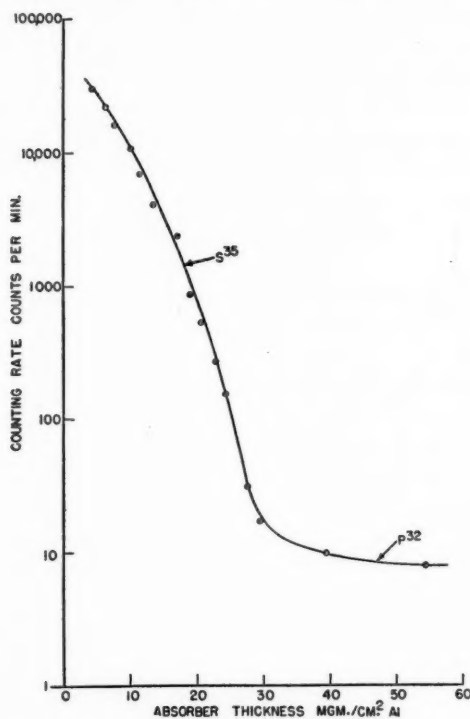


FIG. 5. Activity in stripped ether.

The sharpness of separation emphasizes the usefulness of the solvent extraction technique. It is of interest to note that the P^{32} is present in a form which is extractable to some extent—having a small but measurable partition coefficient. A small amount of S^{35} is taken up by the solvent and is not re-extracted by distilled water. Presumably this is S^{35} present as a sulphur chloride which is soluble in organic solvents.

A visible reddish residue remained on evaporation of the extracted solution, but its weight was less than the limits of sensitivity of the balance (10^{-4} gm.).

Table V summarizes the distribution of material and activity resulting from the above procedure.

TABLE V
SOLVENT EXTRACTION OF 1 GM. IRRADIATED FERRIC CHLORIDE

Solution	Solids content	S^{35} % of original	P^{32} % of original	Fe^{59} % of original
Aqueous residue	10^{-4} gm.	99.5	83	Undetectable
Stripped ether	10^{-3} gm.	0.5	0.01	"
Water extract	Bulk of original $FeCl_3$	Undetectable	17	100

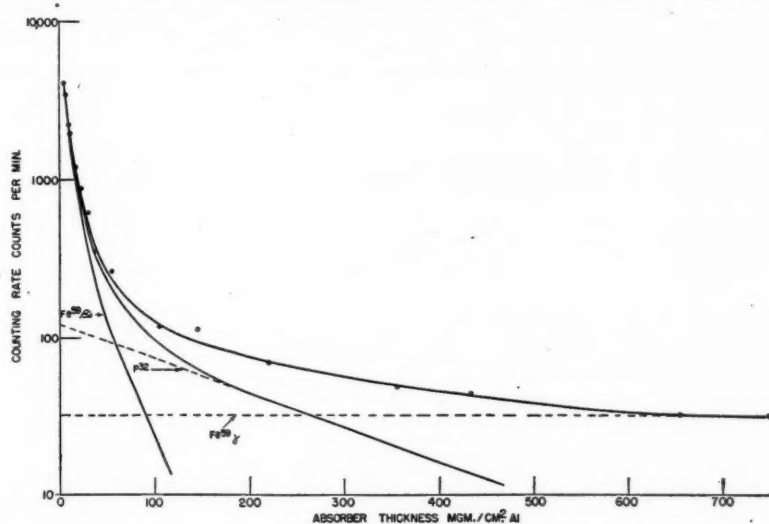


FIG. 6. Activity in water extract.

Assuming (a) 1 mgm. of solids remains per gram of original material, (b) a flux of 5×10^{12} neutrons per $cm.^2$ per sec., (c) the cross section for $Cl^{35}(n, p)S^{35}$ is 0.13 barn, (d) 87.1 days irradiation period, the potential activity concentration would be 100 mc. S^{35} per mgm. total solids—with no inactive sulphur carrier added. The chemical form of the S^{35} in the extracted solution is presumably as $FeS^{35}O_4$. P^{32} formed by side reaction remains as a radioactive contaminant.

Under the conditions outlined above, the Fe^{59} radioactivity would be approximately 80 $\mu c.$ per gm. ferric chloride. Thus, the ratio of $S^{35}:Fe^{59}$ would be about 1000 : 1, in the unextracted material.

For small amounts of ferric chloride (0.1 to 100 gm.) various types of apparatus could be employed to carry out the extraction with a minimum of handling. (1) The two phases could be contacted by a stirrer and the

solvent (top layer) removed by suction, in a series of batchwise extractions. (2) Solvent could be passed countercurrently through a static column of the aqueous solution overflowing at the top to a holding vessel. (3) A Soxhlet type of extractor could be employed, involving recirculation by distillation of a small volume of solvent.

Acknowledgment

Work on the problem of S^{35} preparation and extraction was started under the guidance of Dr. L. Siminovitch. The assistance of Dr. L. Yaffe in the editing of this paper is gratefully acknowledged.

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THE NITROLYSIS OF HEXAMETHYLENETETRAMINE

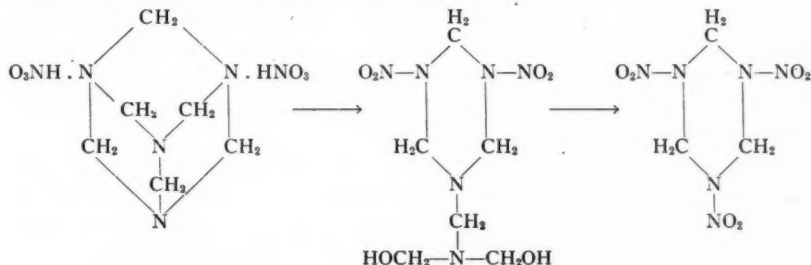
IV. SYNTHESIS OF A CYCLONITE HOMOLOGUE¹

BY G. S. MYERS² AND GEORGE F WRIGHT

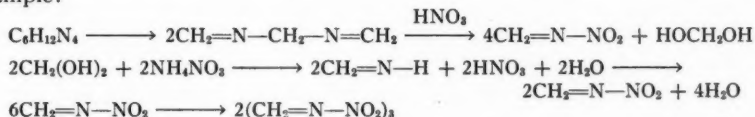
Abstract

A homologue of Cyclonite has been prepared. This homologue, 1,3,6-trinitro-1,3,6-triazacycloheptane was formed by nitrolysis of methylene-*bis*-3,6-dinitro-1,3,6-triazacycloheptane, which was synthesized from *N,N'*-dimethylol-1,2-dinitraminoethane, formaldehyde, and ammonia. The reliability of this synthesis was established by analogous reactions. The nitrolysis yields also 1,8-diacetoxy-2,4,7-trinitro-2,4,7-triazaoctane via 1-acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane. Ammonium nitrate has been shown to promote demethylation in this series just as it does in the triazacyclohexane compounds. Analogies have therefore been drawn between these nitrolyses and that of hexamethylenetetramine. Further comparisons derive from the isolation of 1-acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane and 1-aceto-3,6-dinitro-1,3,6-triazacycloheptane by acetolysis of methylene-*bis*-dinitrotriazacycloheptane with acetic anhydride.

The demonstration that nitrolysis of hexamethylenetetramine (hexamine) forms dimethylolnitramide (3) (or its nitrate ester) as well as Cyclonite has suggested a stepwise nitrolysis mechanism (4),



but one might also advance a fragment mechanism which involved disassembly of hexamine with subsequent reassembly to Cyclonite, for example:



Since the hexamine molecule consists entirely of alternate C—N—C linkages it is difficult to decide between these two mechanisms. Either is logically reasonable on the basis of the symmetrical products containing the C—N—C linkage, which are formed. However if the final product lacked the symmetry of Cyclonite, the probability of reassembly of nitrated fragments to

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give a single cyclic product would be exceedingly remote. We have prepared a homologue of Cyclonite (1,3,5-trinitro-1,3,5-triazacycloheptane) which lacks this symmetry and find that it is not contaminated with Cyclonite. This would suggest, by analogy, that Cyclonite itself is formed by stepwise degradation of hexamine.

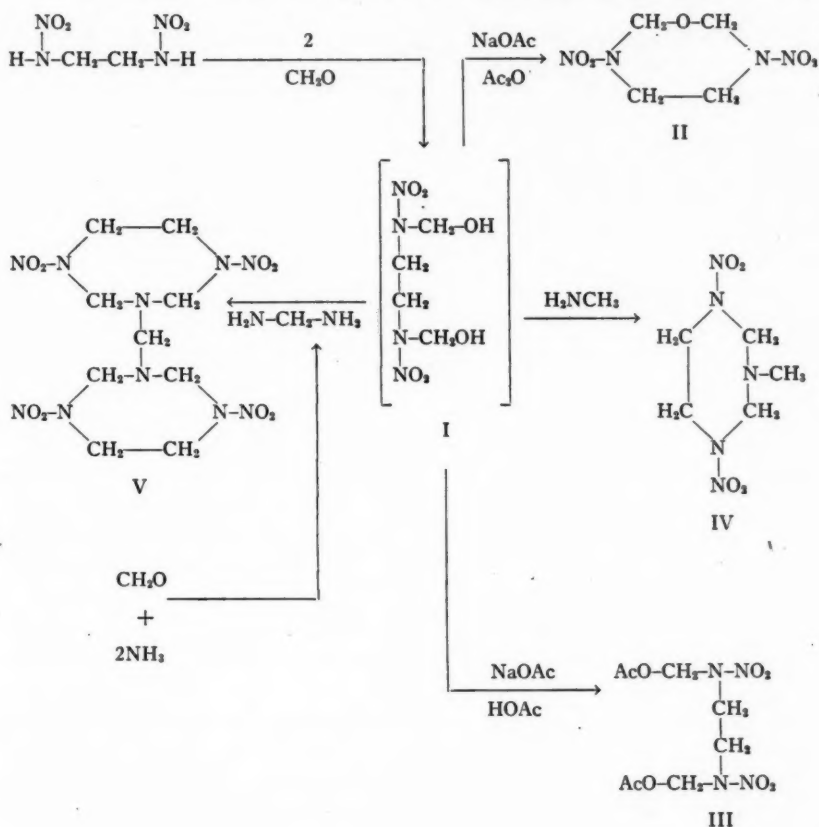
The preparation of compounds containing the triazacycloheptane ring required homologues of the substances synthesized earlier (3) from nitramide formaldehyde, and various amines. This was accomplished simply by utilizing 1,2-dinitraminoethane instead of nitramide. A description of these homologues and their characteristic reaction products forms the basis of the present report.

Since ethylenedinitramine is relatively insoluble in water, the slow solubilization by addition of two equivalents of formaldehyde is strongly indicative of the formation of *N,N'*-dimethylol-1,2-dinitraminoethane, I, even though this compound cannot be isolated. *N*-monomethylol-1,2-dinitraminoethane is always obtained instead (1, 7). The diacetate ester, however, can be prepared by treating the aqueous formaldehyde-ethylenedinitramine solution with sodium acetate and just sufficient acetic anhydride to convert the water to acetic acid. A 63% yield of *N,N'*-diacetoxymethyl-1,2-dinitraminoethane, III, was obtained by heating this solution to 65° C. The same compound can be obtained in 53% yield from *N*-monomethylol-1,2-dinitraminoethane without additional formaldehyde, so that ethylenedinitramine and its two methylol derivatives must represent an equilibrium system involving formaldehyde. This behavior is characteristic also of the formaldehyde-nitramide-dimethylolnitramide system (3).

The formation of the acetate ester, III, was carried out in the acetic acid produced by aqueous hydrolysis of acetic anhydride. If sufficient anhydride is used so that some remains after this water is consumed, the product which has been reported is 1,5-dinitro-3-oxa-1,5-diazacycloheptane, II (7).

There seems, then, to be little doubt that dimethylolethylenedinitramine exists in water solution, and therefore should undergo the same type of condensation observed with dimethylolnitramide (3). Reactions of this type have been observed. When the aqueous solution of I is treated with methylamine a compound precipitates which is 3,6-dinitro-1-methyl-1,3,6-triazacycloheptane, IV, on the basis of analyses, both elemental and functional for methylamine and formaldehyde. Although the compound is not very stable, a hydrochloride can be prepared which accounts for the one basic amino group in the structure.

If, instead of methylamine, a solution of formaldehyde and ammonia is treated with a solution of I, a compound is precipitated which we have specified as methylene-*bis*-3,6-dinitro-1,3,6-triazacycloheptane, V, on the basis of elemental analysis and functional analyses for ammonia, formaldehyde (5), and ethylenedinitramine. The compound largely decomposes in dilute hydrochloric acid, although a small amount can be recovered by neutralization. No salt could be prepared.

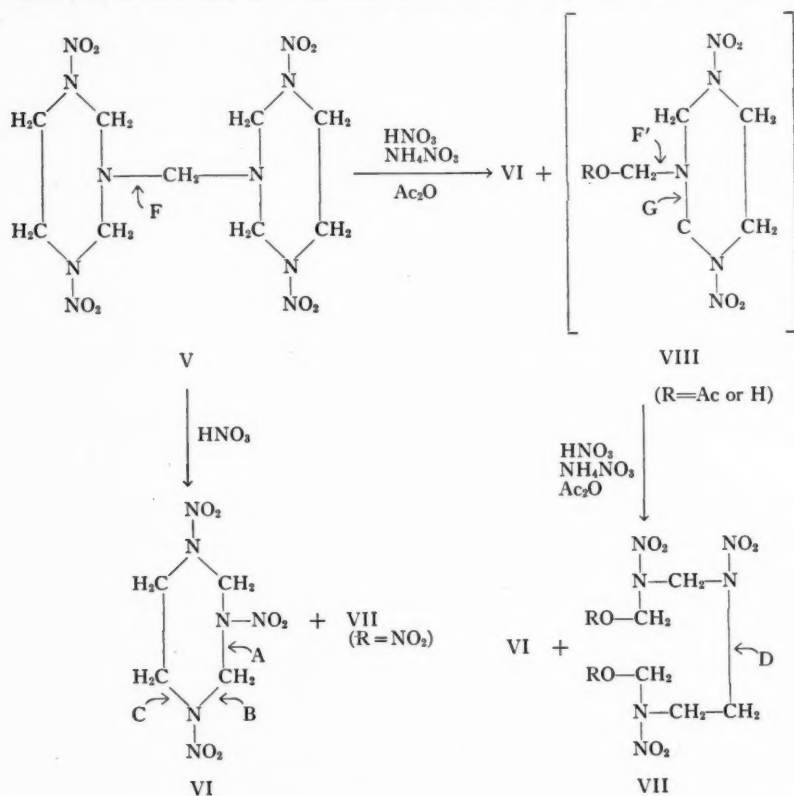


These condensations, as well as those reported previously (3), may be seen to be of the Mannich type, and in this connection it is significant to note that in all such reactions with nitramides, the condensation seems to take place between the nitramide-formaldehyde addition product and the amine, rather than with the free nitramide and the amine formaldehyde addition product.

The formation of many-membered rings seems quite common among these condensations, and no restriction favoring five- and six-membered rings seems to apply when nitrogen is included in the cycle. Indeed the ease with which seven- and eight-membered rings will form in these condensations would seem not to exclude larger cycles, so that one might consider 1,8-*endomethylene*-3,6,10,13-tetranitro-1,3,6,8,10,13-hexaazacyclotetradecane as reasonable a structure for V as the *bis*-triazacycloheptane which has been diagrammed. Either could have formed from the methylenediamine which we consider to be the reaction species in formaldehyde-ammonia (3, 6).

The nitration of V does, however, recommend the triazacycloheptane structure. When methylene-bis-3,6-dinitro-1,3,6-triazacycloheptane, V, is treated at 0° C. with 20 moles of 99% nitric acid and then diluted and neutralized, an impure precipitate is obtained which is probably contaminated with 1,8-dinitroxy-2,4,7-trinitro-2,4,7-triazaöctane, VII (R=NO₂), although we were not able to identify this compound. The isolable product in its crude form was obtained in 76% yield (1 mole V→1 mole VI) if it is 1,3,6-trinitro-1,3,6-triazacycloheptane, VI. Its elemental analysis conforms with this structure.

This Cyclonite homologue, VI, resembles Cyclonite in its solubility in organic solvents, but it is much less stable and, indeed, is destroyed slowly by boiling water (7% in two hours). The marked difference in stability in contrast to



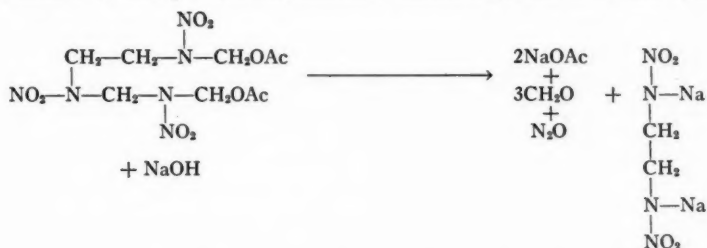
Cyclonite (RDX) or 1,3,5,7-tetranitro-1,3,5,7-tetrazacycloöctane (HMX) finds an explanation when 1,3,6-trinitro-1,3,6-triazacycloheptane, VI, is hydrolyzed by 5% aqueous sodium hydroxide. Decomposition is complete in 10 min. and *no* ethylenedinitramine can be isolated. A control

experiment shows that 97% of ethylenedinitramine itself can be recovered from such alkaline treatment. This must mean that scission of VI occurs at C rather than at A or B. One may infer from this behavior that the methylenedinitramine linkage $\text{—NO}_2\text{N—CH}_2\text{—NNO}_2\text{—}$ is much stronger than homologous alkylenedinitramines. In the event that the ends of a polymeric methylenenitrimine chain ($\text{—CH}_2\text{—[N}_2\text{O}_2\text{—CH}_2\text{]}_n\text{—N}_2\text{O}_2\text{—}$) are blocked with methylenenitramine linkages of like strength, then terminal attack is likewise minimized. This is the situation in the two most stable nitramines, RDX and HMX, which are cyclic; it suggests resonance hybridization.

The preparation of trinitrotriazacycloheptane is somewhat more definitive when methylene-*bis*-dinitrotriazacycloheptane, V, is treated with the reagents used by Bachmann for Cyclonite preparation (2). One mole of V is suspended in 10 moles of acetic anhydride and stirred at 50° to 60° C. while a solution of ammonium nitrate in nitric acid is added over three minutes. The gum which separates after neutralization of the water-diluted mixture can be solvent-separated into a 47% yield of trinitrotriazacycloheptane (1 mole V \rightarrow 1 mole VI) and a second compound, in 43% yield if it were 1,8-diacetoxy-2,4,7-trinitro-2,4,7-triazaöctane, VII (R = Ac). The structure of VII was based on elemental and acetyl analyses.

Although no analyzable derivative of 1,8-diacetoxy-2,4,7-trinitro-2,4,7-triazaöctane, VII, has been obtained, the compound yields, with 98% nitric acid at 0° to 5° C., a product which is evidently VII (R = NO₂). This product is so unstable that it decomposes after a few minutes at room temperature. This instability precludes its possible conversion to the dimethoxy derivative, (VII) (R = CH₃), since this reaction involves warm methanol. The crude material was, however, reconverted in 40% yield to VII (R = Ac) by treatment with sodium acetate in acetic acid at room temperature. This excludes an alternative structure for VII (R = Ac) such as 9-acetoxy-8-nitroxymethyl-3,6-dinitro-3,6,8-triazanonane-2, because nitration followed by acetylation would not have regenerated the original compound.

The alkaline hydrolysis of 1,8-diacetoxy-2,4,7-trinitro-2,4,7-triazaöctane, VII, yields only 82% of the ethylenedinitramine expected from the equation



This would indicate that the terminal acetoxy groups have prevented degradation from the ends of the alkylenedinitramine structure to an extent somewhere

between that in VI, where total destruction of the ethylenedinitramine occurred, and that in V where none of the constituent ethylenedinitramine is destroyed. This indication is, of course, based on the assumption that if degradation cannot occur *toward* the integral ethylenedinitramine linkage (that is, from the ends of a chain of atoms) then scission will occur such as is illustrated at D in VII.

Thus far in this report the scission products of methylene-*bis*-dinitrotriazacycloheptane, V, have resulted from media involving nitric acid. However acetic anhydride alone splits the compound, although somewhat more slowly than does nitric acid. A six hour period of boiling with the anhydride in acetic acid produces the expected two compounds. The less soluble 1-acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane (VIII, R=Ac) precipitates from the cold reaction mixture. The lesser yield of 1-aceto-3,6-dinitro-1,3,6-triazacycloheptane may be attributed to its greater solubility in the acetic acid medium where impurities prevent its separation.

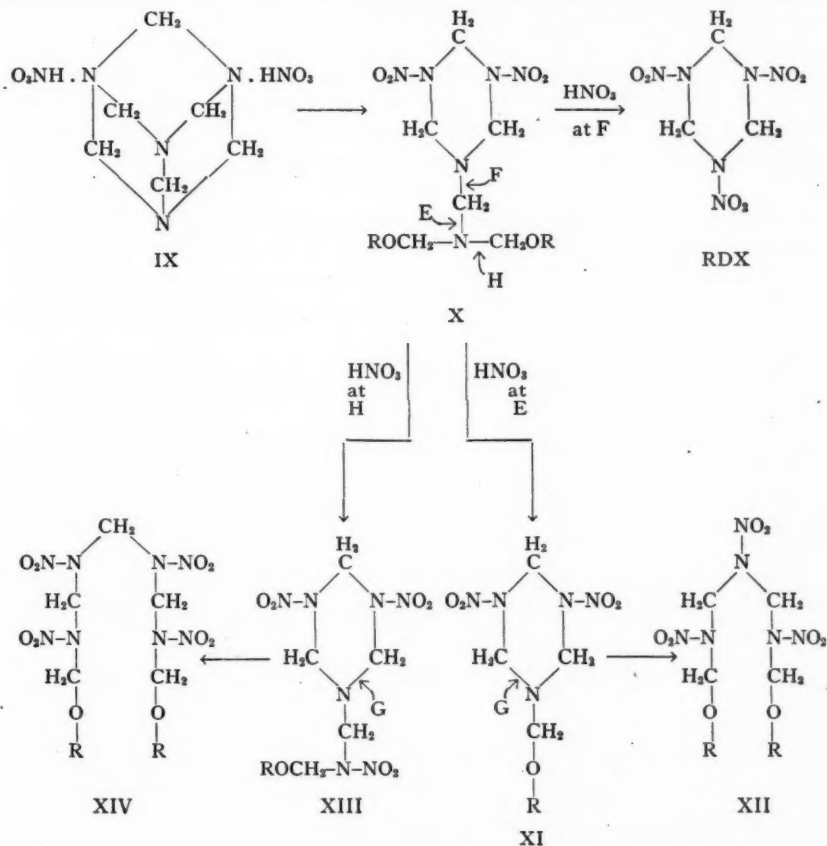
The acetoxymethyl group in acetoxymethyldinitrotriazacycloheptane (VIII, R=Ac) is extremely labile and is converted either to the analogous propyl ethers (VIII, R=C₃H₇) or the ethyl ether (VIII, R=C₂H₅) by crystallization from the requisite alcohol. The ethoxymethyl compound can be converted by treatment with 99% nitric acid to trinitrotriazacycloheptane, VI, in small (6%) yield. Because of the lability of the pendulous group one might expect replacement of the acetoxymethyl group by nitro, via demethylation, at F' (structure VIII) upon treatment with the Bachmann reagents, acetic anhydride, ammonium nitrate, and nitric acid. Indeed this occurs at 60° C., but trinitrotriazacycloheptane is not the only product. Scission of the ring also occurs at G as shown in structure VIII to give 1,8-diacetoxy-2,4,7-trinitro-2,4,7-triazaöctane, VII (R=Ac). According to the relative amounts of product which were obtained, 73% of the scission occurs at F' and 27% at G.

It is probably unsafe to evaluate the relative strengths of the linkages in V and VIII (R=Ac) on the basis of the 52 : 48 ratio versus the 73 : 27 ratio of trinitrotriazacycloheptane VI to diacetoxytrinitrotriazaoctane, VII, obtained respectively from the two compounds. Firstly there is no assurance that R is not partly NO₂ when VIII is a transient intermediate in the conversion of V to VI and VII. Secondly the lesser total yields obtained from methylene-*bis*-dinitrotriazacycloheptane, V, would indicate a high ammonium nitrate consumption by the formaldehyde freed because of side reactions. If ammonium nitrate is actually the reagent responsible for demethylation, then demethylation to produce trinitrotriazacycloheptane would be decreased in nitrolysis of V as compared with nitrolysis of VIII because relatively less of the reagent would be available over the reaction life of V than it would be during the more efficient nitrolysis of VIII.

The latter assumption that ammonium nitrate is the demethylation agent seems quite reasonable in view of the fact that acetoxymethyldinitrotriazacycloheptane, VIII, yields no isolable amount of trinitrotriazacycloheptane, VI, when it is treated with acetic anhydride and nitric acid in absence of

ammonium nitrate. Under these conditions scission seems to take place principally at G to give an 82% yield of diacetoxytrinitrotriazaoctane, VII.

On the basis of these data, and the compounds which have been isolated, the mechanism of nitration of methylene-*bis*-dinitrotriazacycloheptane, V, seems to be first a scission at F to produce VI and the transient fragment VIII. The fate of this fragment will depend on the available amount of ammonium nitrate to demethylolate it at F' in order to form more trinitrotriazacycloheptane, VI, since otherwise scission will occur at G to give VII (R = Ac.). No other structures are possible except one which places two nitro groups on one nitrogen (such structures are unknown) or one in which a reversed fission has produced a nitroxy-acetamide compound. The latter behavior is unknown, but it would still involve fission at G. The final alternative, 9-acetoxy-8-nitroxymethyl-3,6-dinitro-3,6,8-triazanonanone-2 would not be expected to give the precise acetyl values which were obtained for VII (R = Ac) nor could it have been nitrated and then reacetylated to be regenerated in its original form.



In so far as analogies between triazacyclohexane and triazacycloheptane rings are valid, one can assume that when hexamine dinitrate, IX, nitrolyzes to form the primary scission product, X, the subsequent scission is probably largely at F with lesser amounts at E and H to account for the limited amounts of by-products such as XII via XI, and XIV via XIII when esterification occurs at E or H. While such a concept does not preclude a stepwise demethylation (down to linkage F) of nonesterified X, it excludes XI as a significant intermediate in the formation of RDX. This follows by analogy with the triazacycloheptane chemistry reported here, since XI might be expected to split appreciably at position G. This exclusion of XI as intermediate applies only to the reaction where demethylation can proceed normally. When esterification is promoted strongly and demethylation is correspondingly retarded, the scissions at H and especially at E may become preponderant.

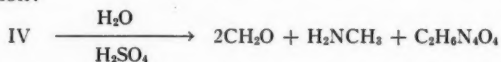
Experimental*

3,6-Dinitro-1-methyl-1,3,6-triazacycloheptane, IV

Finely ground ethylenedinitramine, weight 9.0 gm. (0.06 mole) was suspended in 18.4 cc. (0.24 mole) of 37% formalin. The slurry was warmed to 60° C. and stirred for 11 min. until solution was complete. After five minutes longer at 60° C., the solution was cooled to 0° C. No insoluble material appeared at this stage. A 30% aqueous methylamine solution, 12.4 cc. (0.12 mole), was added dropwise with cooling to the reaction mixture over a three minute period. The white crystalline precipitate which formed almost at once was further agitated for 20 min. at 0° C. and then filtered off. The product, washed with 300 cc. water and dried at 50° C., weighed 10.23 gm. (83% theory, ethylenedinitramine basis) and melted at 158° to 160° C. with frothing.

Dinitromethyltriazacycloheptane is insoluble in water, dilute alkali, cold ethanol, and ether but is soluble in hot benzene, acetic acid, and ethyl acetate and in cold acetone, methyl ethyl ketone, and nitromethane. It is fairly stable in warm solvents and is purified easily from hot ethyl acetate from which it separates on cooling in needlelike crystals, m.p. 159° C. Calc. for $C_6H_{11}N_5O_4$: C, 29.2; H, 5.42; N, 34.1%. Found: C, 29.5; H, 5.44; N, 34.0%.

Formaldehyde and methylamine analysis, carried out according to the method of Meyer (5) were both higher than would be expected from the following equation:



However, when ethylene dinitramine was carried through the same analytical procedure it indicated a content of 17.1% formaldehyde and 3.0% ammonia. The formaldehyde analysis on IV was found to be 43.6%; the methylamine

* All melting points have been corrected against reliable standards.

was 20.2%. If the ammonia and formaldehyde values for the ethylenedinitramine content of IV are subtracted, then percentages are obtained which are in fair agreement with the calculated value. Calc. for $C_5H_{11}N_5O_4$: $2CH_2O$, 29.3; CH_3NH_2 , 15.1%. Found: $2CH_2O$, 31.1; CH_3NH_2 , 16.1%.

We were unable to prepare a picrate of dinitromethyltriazacycloheptane but the hydrochloride was prepared by addition of dry hydrogen chloride to a solution of 0.30 gm. (0.00147 mole) of IV in 30 cc. benzene until precipitation was complete. The salt was filtered, benzene washed, and dried at 50° C. It weighed 0.29 gm. (80% of theoretical) and melted at 138° to 140° C. with violent frothing. An otherwise similar preparation in acetone gave a yield of only 8%, and the decomposition product, ethylenedinitramine, was found in large quantity in the solution. Calc. for $C_5H_{12}N_5O_4Cl$: C, 24.9; H, 5.01; N, 29.0%. Found: C, 25.4; H, 4.86; N, 28.5%.

Methylene-bis-3,6-dinitro-1,3,6-triazacycloheptane, V

A suspension of 138 g. (0.90 mole) of ethylenedinitramine in 275 cc. (3.60 mole) of 37% formalin was warmed to 60° C. with stirring. The ethylenedinitramine went into solution in five minutes. After 15 min. longer at 60° C., it was cooled to 20° C., then 245 cc. (3.60 moles) of 28% ammonia was added over a 20 min. period. The temperature was maintained at 20° to 40° C. with an ice bath. The sticky viscous solid which separated was difficult to stir, but when ground in a mortar, it solidified to a white amorphous solid which subsequently was stirred with 1500 cc. of water at 25° C. for one hour. After filtration and drying at 50° C., it weighed 110 gm. (63% on ethylenedinitramine basis) and melted at 197° to 198° C. (soft 196° C.). When the initial formaldehyde addition was increased to 7.2 moles the yield was raised to 94%.

The compound is insoluble in hot ethyl acetate, ethanol, benzene, acetic acid, and 10% sodium hydroxide. It is soluble in warm acetone and ethyl methyl ketone and also in cold concentrated and dilute hydrochloric acid. It can be purified by solution in warm acetone and precipitation with petroleum ether (b.p. 60° to 70° C.) to yield small white crystals, m.p. 205° C. (brown, decomp.). Calc. for $C_9H_{18}N_{10}O_8$: C, 27.5; H, 4.59; N, 35.0%. Found: C, 27.6; H, 4.59; N, 35.0%. The formaldehyde and ammonia analyses were CH_2O , 53.1%, and NH_3 , 13.3%. When these were corrected for the blank with pure ethylenediamine they became CH_2O , 40.1%; NH_3 , 11.0%. The calculated values (1 mole V gives $5CH_2O$ and $2NH_3$) are: CH_2O , 38%; NH_3 , 8.6%. The deviations are undoubtedly owing to the erratic hydrolysis of ethylenedinitramine in dilute sulphuric acid.

1,3,6-Trinitro-1,3,6-triazacycloheptane, VI

To 25 cc. (0.60 mole) of 99% nitric acid which was cooled to 2° C. in a three-necked flask was added, with stirring, 10 gm. (0.026 mole) of finely ground methylene-bis-dinitrotriazacycloheptane, V, over a 15 min. period. The reaction temperature which was held at 2° to 4° C. with an ice-salt bath during the addition, was maintained at 0° C. during the subsequent stirring period of 90 min. The content of the flask was then drowned in 500 cc. of ice and water

and this slurry was neutralized to pH 6 with 28% ammonia. Although 1.57 gm. of the precipitate was a solid, m.p. 134° to 138° C., the greater part was a gum which was converted to 3.10 gm. of powder, m.p. 152° to 153° C. (soft 150° C.) by stirring for five hours at 25° C. with 25 cc. of 95% ethanol. The total weight of crude (4.67 gm.) might be considered as a 38% yield if 1 mole of methylene-bis-dinitrotriazacycloheptane were nitrated to 2 moles of trinitrotriazacycloheptane.

A second preparation was carried out identically except that 40 equivalents (instead of 20 equivalents as above) of nitric acid were used per mole of slightly impure V (m.p. 198° to 199° C.). It was found that the gummy crude material could be purified equally well by washing with acetone or cooking with methanol. The total yield of trinitrotriazacycloheptane was 9.77 gm., m.p. 161° to 163° C. or 16.5% on the 1 mole to 2 mole basis. No other product could be discovered in the purifying solutions.

Trinitrotriazacycloheptane is insoluble in warm ethanol, benzene, acetic acid, chloroform, and ether but is very soluble in acetone, methyl ethyl ketone, nitromethane, and dioxane. The compound is decomposed by boiling in water, but can be crystallized by solution in hot acetone to which is then added petroleum ether (b.p. 60° to 70° C.). Two polymorphs are obtained, one (α) is a heavy prismatic crystal, the other (β) short and acicular. Both melt at 165° to 165.5° C. with decomposition, when they are separated mechanically. Calc. for $C_4H_8N_6O_6$: C, 20.4; H, 3.44; N, 35.6%. Found: C, 20.4; H, 3.41; N, 35.6%.

1,8-Diacetoxy-2,4,7-trinitro-2,4,7-triazaöctane, VII, (R=Ac)

A suspension of 2.0 gm. (0.005 mole) of finely ground methylene-bis-dinitrotriazacycloheptane, V, in 5.1 cc. (0.051 mole) of acetic anhydride was stirred, initially at 60° C. while a solution of 0.48 gm. (0.0060) mole of ammonium nitrate in 0.51 cc. (0.012 mole) of 99% nitric acid was added over a three minute period. A cooling bath maintained the reaction between 60° and 70° C. After 20 min. subsequently at 60° C. the whole was drowned in 150 cc. of ice-water mixture. The slurry was immediately neutralized to pH 6 by addition of 28% ammonia; the sticky mass of solid which settled out was filtered off and suspended in ethanol for 12 hr. This ethanol treatment converted the gum to a granular precipitate which was filtered off, washed with ether, and dried at 50° C. It weighed 1.83 gm. and melted at 115° to 130° C. (soft 105° C.). This crude product was separated by solution in warm acetone and precipitation into petroleum ether (b.p. 60° to 70° C.) to give trinitrotriazacycloheptane VI, m.p. 162° to 163° C. (47% yield, 1 : 1 basis, estimated from these crystallizations), and a second compound melting at 97° to 98° C. after repeated acetone-petroleum ether crystallizations 56 \rightarrow 20° C. Estimated yield was 43% on the 1 : 1 basis. This second compound seems, according to its analyses, to be diacetoxytrinitrotriazaoctane, VII, (R=Ac). Calc. for $C_9H_{10}N_6O_{10}$: C, 29.4; H, 4.37; N, 22.8; CH_3CO , 23.4%. Found: C, 29.5; H, 4.35; N, 22.7; CH_3CO , 22.8%.

1,8-Dinitroxy-2,4,7-trinitro-2,4,7-triazaöctane, VII, (R=NO₂).

To 7 cc. (0.016 mole) of 98% nitric acid at 0° C. was added with shaking 1 gm. (0.00272 mole) of VII (m.p. 97° to 98° C.) over four minutes. The resulting solution was kept at 0° C. for seven minutes longer and then drowned in 10 parts ice-water mixture. A fluffy white solid separated out. A melting point could not be taken since this product became sticky on removal from the medium. It could not be purified from dioxane, carbon tetrachloride, or acetone. The absence of any unnitrated VII in this product was demonstrated by allowing the crude material to stand at 5° C. in 10 cc. of water to which a few drops of ammonia had been added. After two days at this temperature the material had decomposed and no water insoluble material remained. A test portion of VII (R=Ac) survived this treatment, so none of the acetate ester was present in the damp product.

The damp product obtained by this ester-interchange of VII with nitric acid was suspended in a solution of 1 gm. sodium acetate in 10 cc. acetic acid and 4 cc. acetic anhydride at 25° C. It dissolved completely in 15 min. The resulting solution was allowed to stand for 20 hr. and then drowned in water. The gummy suspension was extracted with 40 cc. ethyl acetate, the extract washed twice with water and concentrated to dryness *in vacuo*. The residue was dissolved in 5 cc. acetone-methanol and the solvent allowed to evaporate slowly over four days. The crystal crop weighed 0.40 gm. and melted at 82° to 87° C. This crude 40% yield was crystallized from acetone-ethanol to melt at 96° to 97° C. A mixed melting point with VII (R=Ac) was not lowered.

Methylene-bis-3,6-dinitro-1,3,6-triazacycloheptane with Acetic Anhydride

A suspension of 0.2 mole (78.8 gm.) crude methylene-bis-dinitrotriazacycloheptane (m.p. 185° C.) in 0.4 mole (40 cc.) of acetic anhydride and 400 cc. of glacial acetic acid was boiled under reflux for eight hours and then filtered to remove insoluble material. From the cooled filtrate there precipitated 32.4 gm. of material melting at 183° to 184° C. This was crystallized from 350 cc. of boiling acetic acid to yield 29.1 gm., m.p. 182.7° to 183.7° C. Recrystallization (15 cc. per gm.) from the same solvent did not raise this melting point. Yield of the crude 1-acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane (VIII, R=Ac) is 55% of theoretical (1 : 1 molar basis). Calc. for C₇H₁₃N₃O₆: C, 31.9; H, 4.98; N, 26.6%. Found: C, 32.2; H, 5.05; N, 26.5%.

The filtrate from which crude VIII was removed was diluted with 750 cc. of ether. After two days this was filtered to remove a gummy solid melting roughly at 144° C., which was dissolved in 25 cc. of hot nitromethane. On cooling, 4.23 gm. precipitated, m.p. 153° to 153.5° C. Dilution of the filtrate with 30 cc. ether yielded 3.20 gm. more, melting above 150° C. The total crude yield was 16% of theoretical. This 1-aceto-3,6-dinitro-1,3,6-triazacycloheptane was purified in 58% recovery from boiling nitromethane (1.6 cc. per gm.) to melt at 153.8° to 154.2° C. No water insoluble product was isolated after this compound was dissolved in 95% nitric acid for one hour. Calc. for C₆H₁₁N₃O₅: C, 30.9; H, 4.76; N, 30.1%. Found: C, 31.1; H, 4.80; N, 30.3.

1-Ethoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane

When 0.019 mole (4.98 gm.) of 1-acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane was dissolved in 205 cc. of boiling absolute ethanol over 10 min. the filtered solution when cooled yielded 3.32 gm. of needles melting at 165.8° to 166.4° C. or 70% of theoretical. Crystallization from 13 cc. ethanol plus 18 cc. acetic acid gave a 75% recovery of material melting at 166.2° to 166.4° C. This melting point was not raised by recrystallization from boiling absolute ethanol (37 cc. per gm.) to give a 79% recovery. Calc. for $C_7H_{15}N_3O_6$: C, 33.7; H, 6.06; N, 28.2%. Found: C, 33.8; H, 6.04; N, 28.1%.

The reaction is more conveniently carried out if 20 cc. each of absolute ethanol and glacial acetic acid are used instead of the 205 cc. of ethanol alone. The yield is slightly higher (78%) than when ethanol alone is used.

A 0.27 gm. sample of the ethoxymethyl compound after boiling with 4 cc. of 5% aqueous sodium hydroxide for eight minutes yielded, after acidification with hydrochloric acid to pH 1, 0.17 gm. or 63% of its weight of ethylene-dinitramine (theory requires 60.3%).

When 1.25 gm. (0.005 mole) of this ethoxymethyldinitrotriazacycloheptane was added to 4.6 cc. (0.055 mole) of 99% nitric acid at -45° C. it dissolved completely. After warming to 25° C. over five minutes, it was poured into ice and neutralized with ammonia. The precipitate weighed 0.15 gm. and melted at 110° to 164° C. This was dissolved in 3 cc. hot acetone and cooled to precipitate a compound, not yet identified, which was filtered off and melted at 189.5° to 190.5° C. The filtrate was fractionally precipitated by addition of petroleum ether (b.p. 60° to 70° C.) to yield 0.07 gm. which melted from 140° to 162° C. This was crude trinitrotriazacycloheptane, VI, (6% yield), which was identified, after purification from 1 : 1 acetone - petroleum ether, by melting point (165.5° C.) and mixed melting point with an authentic sample.

1-Propoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane

The normal propyl ether (m.p. 136.8° to 138.2° C.) or the isopropyl ether (m.p. 182.2° to 184.6° C.) were formed more easily than the ethyl ether by repeated crystallizations of acetoxymethyldinitrotriazacycloheptane from the appropriate alcohol. Calc. for $C_8H_{17}N_3O_6$: C, 36.5; H, 6.49; N, 26.6%. Found for normal ether: C, 36.2; H, 6.32; N, 26.6%. Found for iso ether: C, 36.8; H, 6.49; N, 26.2%.

Nitrolysis of 1-Acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane, VIII

A. With acetic anhydride - nitric acid.—A suspension of 2.63 gm. (0.01 mole) acetoxymethyldinitrotriazacycloheptane in 10.4 cc. (0.102 mole) of acetic anhydride and 0.46 cc. (0.011 mole) of 99% nitric acid was stirred for four hours at 25° C., then 30 min. at 50° C. The reaction mixture, poured into ice and neutralized with 25 cc. of aqueous ammonia, yielded 2.97 gm. (82% of theoretical) of diacetoxyltrinitrotriazaoctane, VII ($R=Ac$), melting at 91° C., with prior softening. Solution of this crude product in 7 cc. acetone

yielded on dilution with petroleum ether (b.p. 60° to 70° C.) 2.22 gm. in three successive crops melting at 98° C., 97.5° C., and 96.5° C. None of the trinitrotriazacycloheptane could be discovered.

B. With acetic anhydride - nitric acid - ammonium nitrate.—A slurry of 9.96 gm. (0.038 mole) of acetoxymethyldinitrotriazacycloheptane in 20.8 cc. (0.204 mole) of acetic anhydride was stirred at 60° C. while 1.92 gm. (0.024 mole) of ammonium nitrate in 2.04 cc. (0.048 mole) of 99% nitric acid was added over 15 min. After 20 min. subsequent stirring the whole was poured into ice and neutralized with 38 cc. of aqueous ammonia. The solidified gum, after two hours, was filtered; it weighed 11.7 gm. and melted below 90° C. This was dissolved in acetone and fractionally precipitated with petroleum ether (b.p. 60° to 70° C.) to yield first trinitrotriazacycloheptane and then diacetoxyltrinitrotriazaoctane in approximately equal amounts. These amounts correspond to yields of 65% and 25% respectively.

C. With nitric acid - ammonium nitrate.—A solution of 1 gm. (0.0038 mole) of acetoxymethyldinitrotriazacycloheptane in a solution of 7.5 gm. (0.094 mole) of ammonium nitrate in 5.6 cc. (0.14 mole) of 99% nitric acid was let stand one day, then poured into ice and filtered to remove 0.12 gm. of impure trinitrotriazacycloheptane (m.p. 149° to 162° C.). This 13% crude yield was purified from acetone - petroleum ether (b.p. 60° to 70° C.) to melt at 166° C. A mixed melting point with authentic material was not lowered.

Liberation of Ethylenedinitramine by Alkaline Hydrolysis

A 1 gm. quantity of the nitramine to be analyzed was suspended in 12 cc. (0.015 mole) of 5% aqueous sodium hydroxide and boiled for 20 min., at which time decomposition was complete. The hydrolyzate was acidified to pH 1-2 with concentrated hydrochloric acid. After 12 hr. at 6° C., the precipitated ethylenedinitramine was filtered, water-washed, and dried at 110° C. The acid filtrate was evaporated to dryness under 12 mm. and a further yield was extracted from the residue with acetone and thus recovered upon evaporation. The total ethylenedinitramine was then weighed and its melting point found to be 175° to 177° C., in all cases.

Under these conditions ethylenedinitramine was itself recovered in 97% yield, while methylene-bis-3,6-dinitro-1,3,6-triazacycloheptane, V, produced 98% of that amount expected on the basis of the structure. On the other hand 1,8-diacetoxy-2,5,7-trinitro-2,5,7-triazaoctane, VII, yielded only 82% of the expected ethylenedinitramine, while 1,3,6-trinitro-1,3,6-triazacycloheptane gave none at all.

Monomethylethylenedinitramine

A solution of one mole ethylenedinitramine in 2 moles of aqueous 40% formalin was treated with a drop of pyridine and 3.5 moles of acetic acid. After two hours at 25° C., a 67% yield of crude monomethylethylenedinitramine separated, m.p. 124° to 126° C.

When an excess of formaldehyde was used, the same product was obtained. Through a solution of 15 gm. (0.1 mole) of ethylenedinitramine in 40 cc. of

ethanol was bubbled 12 gm. (0.4 mole) of gaseous formaldehyde from paraform. When the temperature had subsided, the solution was cooled to yield 4.6 gm. of product, m.p. 126° C. Evaporation of the ethanol left 12.7 gm. more of product. The whole was crystallized from water at 80° C. to give 91% yield, m.p. 127° C. Calc. for $C_8H_8N_4O_5$: C, 20.0; 4.44; N, 31.1%. Found: C, 20.1; H, 4.43; N, 31.0%.

Prolonged heating in water caused evolution of formaldehyde. Attempted crystallization from hot acetone or methyl, ethyl, and butyl alcohols yielded only ethylenedinitramine. The compound is insoluble in ether, chloroform, methyl, or ethyl alcohol but is moderately soluble in acetone.

All variations of these two methods have failed to yield a compound identifiable as dimethylolethylenedinitramine, I.

1,5-Dinitro-3-oxa-1,5-diazacycloheptane, II

A solution of 0.15 gm. (0.001 mole) of ethylenedinitramine in 0.15 cc. (0.002 mole) of 40% formalin was treated at 20° C. with 0.015 mole (1.5 cc.) of acetic anhydride. The resulting solution warmed to 35° C. on standing at room temperature. It was then digested at 65° C. for 25 min., diluted with 8 cc. of water and the precipitate filtered, water-washed, and dried at 50° C. Weight of product was 45 mgm., m.p. 145° to 148° C. (shrinkage 72° C.). Yield calculated as crude 3,6-dinitro-1-oxa-3,5-diazacycloheptane was 23% of theory (ethylenedinitramine basis). Three crystallizations from warm acetone - petroleum ether solution raised the melting point to 154°-155° C. Calc. for $C_4H_8N_4O_5$: C, 25.0; H, 4.17; N, 29.2%. Found: C, 25.7; H, 4.46; N, 29.1%.

N,N'-Diacetoxymethylethylenedinitramine, III

A solution of 15 gm. (0.1 mole) of ethylenedinitramine in 16.25 cc. (0.2 mole) of 40% formalin was prepared by solution at 60° C. To this was added 9 gm. (0.11 mole) of sodium acetate and 60 cc. (0.57 mole) of acetic anhydride. The resulting slurry was digested at 65° C. for one hour. Dilution with 250 cc. of water precipitated 18.2 gm. overnight, m.p. 78° to 80° C. or 63% of theoretical. Crystallization from ethanol - petroleum ether raised this melting point to 83° C. Calc. for $C_8H_{14}N_4O_8$: C, 32.6; H, 4.77; N, 19.0%. Found: C, 33.0; H, 4.72; N, 18.9%.

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NITROLYSIS OF HEXAMETHYLENETETRAMINE

V. 1,7-DINITROXY-2,4,6-TRINITRO-2,4,6-TRIAZAHEPTANE AND RELATED COMPOUNDS¹

By W. J. CHUTE,² A. F. MCKAY, R. H. MEEN, G. S. MYERS,³ AND
GEORGE F WRIGHT

Abstract

When hexamethylenetetramine is nitrolyzed with nitric acid and an anhydride in absence of ammonium nitrate the synthesis of cyclic nitramines is decreased and the yields of esterified linear tetramethylenetrinitramines are increased. The two remaining carbon atoms and one nitrogen atom in hexamine can be accounted as esterified dimethylolnitramide. The isolation of a trace of linear pentamethylenetetranitramine from a normal nitrolysis of hexamethylenetetramine shows that in all of these reactions a common intermediate, dimethylolaminomethyldinitrotriazacyclohexane, must be present. This has never been isolated, but its reactions can be deduced from the behavior of methylene-bis-3,5-dinitro-1,3,5-triazacyclohexane.

The normal Hale nitrolysis of hexamine with 99.6% nitric acid (8) yields chiefly Cyclonite and dimethylolnitramine (6). It has been shown (9) that if the nitrolyzing agent, nitric acid, is supplemented by an acid anhydride, the course of nitrolysis can be changed in the case of 1,5-*endomethylene*-3,7-dinitro-1,3,5,7-tetrazacyclooctane (DPT), unless ammonium nitrate is present. We sought to test the theoretical consequences of this variation on hexamine itself.

Bachmann (3) has found that when hexamine is treated at room temperature with a mixture of nitric acid and acetic anhydride (1 : 1.2 moles) no Cyclonite is formed, but a fair yield of compound is produced for which the structure 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, III, was proposed (11).

When the ratio of nitric acid to acetic anhydride is changed to 1 : 0.45 (nitric now being in excess) a low yield of Cyclonite is now formed, but it contains an impurity, not III, and too unstable for easy isolation. The impurity can, however, be converted to 1-acetoxy-7-ethoxy-2,4,6-trinitro-2,4,6-triazaheptane, V, by boiling in ethanol. The previous demonstration (9) that the nitroxymethylenenitramine linkage ($\text{NO}_2\text{CH}_2\text{—N—NO}_2$) is easily convertible to alkoxymethylenenitramine ($\text{RO—CH}_2\text{—N—NO}_2$) thus designates the impurity as 1-acetoxy-7-nitroxy-2,4,6-trinitro-2,4,6-triazaheptane (pro-V).

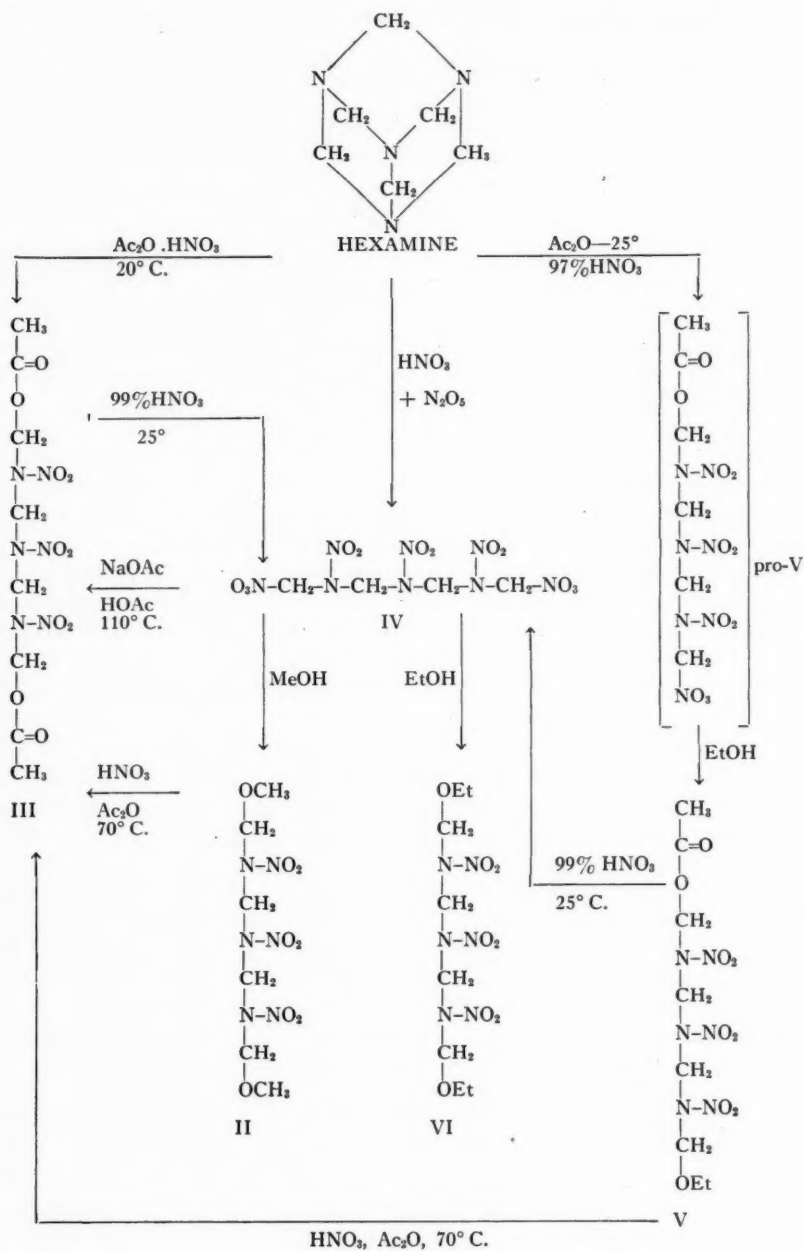
When either the 1,7-diacetoxy compound III or the 1-acetoxy-7-ethoxy compound V is treated with nitric acid, it is converted to 1,7-dinitroxy-2,4,6-trinitro-2,4,6-triazaheptane, IV. The identity of this compound follows from its conversion to either 1,7-dimethoxy-(II) or 1,7-diethoxy-2,4,6-trinitro-2,4,6-triazaheptane (VI) by heating with the appropriate alcohol. The

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dinitroxy compound IV can also be converted to the diacetoxo compound III by the sodium acetate-acetic acid treatment previously described (9). Finally, II and VI can be converted to the diacetoxo compound III by treatment with acetic anhydride containing enough nitric acid to oxidize the alkoxy radicals. Advantage has therefore been taken of the easy interconvertibility of nitraminomethylene ethers and esters to establish an interrelated series of compounds of identical skeletal type.

When hexamine is treated with the nitric acid-nitrogen pentoxide mixture equivalent to nitric acid with apparent strength of 106%, the yield of Cyclonite is lowered appreciably. This is not owing to a destructive action of the pentoxide, because a normal nitrolysis, to which nitrogen pentoxide is subsequently added, gives a normal yield of Cyclonite (and DPT, on neutralization) with little other by-product formation.

The Cyclonite produced from the 106% nitric acid contains an unstable impurity, which must be 1,7-dinitroxy-2,4,6-trinitro-2,4,6-triazaheptane IV, because cooking with methanol produces a 22% yield of 1,7-dimethoxy-2,4,6-trinitro-2,4,6-triazaheptane, II.

Three nitrolyses of hexamine have thus been outlined which yield esters when anhydrides are present. In two of these no other compound indicative of reaction mechanism could be isolated, probably because of difficulty in manipulation of the unstable and dangerous complex reaction product. The third, however, which converted hexamine to 1,7-diacetoxo-2,4,6-trinitro-2,4,6-triazaheptane, III, in 51% yield, also produced a 39% yield (1:1 basis) of diacetoxodimethylnitramide VII in spite of some decomposition during distillation. We assume that III and VII were present approximately in equimolar amounts.

It is evident that the tetramethylenetriamine skeleton is formed in all three reaction mixtures containing anhydride. The following scheme suggests how this tetramethylenetriamine structure is formed.

The first nitrolyses at A would yield the intermediate VIII, which in absence of anhydride would undergo demethylation and, finally, nitrolysis at F to give Cyclonite (RDX). In presence of anhydrides, however, the free hydroxyl groups in VIII would tend to be esterified to form X. This esterification would hinder demethylation. The isolation of VII in the preparation of 1,7-diacetoxo-2,4,6-trinitro-2,4,6-triazaheptane, III ($R, R' = \text{Ac}$), indicates that the next nitrolysis occurs at E in X to leave the compound XI. The latter has been reported as its ethyl ether (evidently via the nitrate ester) in low temperature nitrolysis of hexamine (5), but its survival in the anhydrous reaction mixture would not be expected; it would either nitrolyze at F to give Cyclonite (RDX) with demethylation, or else it would esterify in presence of anhydride to give XII. This esterification would hinder demethylation and permit the final attack by nitrolysis at G to open the ring. Subsequent esterification would yield one of the three compounds III, IV, and pro-V which are produced by reaction mixtures rich in anhydride.

decomposition evidently involves decomposition of part of the PCX base to formaldehyde at such a rate that it can condense with more amine to give XVII. The constitution of the product was first recognized in the present work by its elemental analysis for nitrogen and by a molecular weight determination of a value, 320, which was closer to 360 (calculated for XVII) than was 207 (calculated for XI). The earlier workers (5) had ascertained the existence of the cyclotrimethylenetriamine cycles by conversion to 1-aceto (1), XX, and 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane (4) but these methods did not produce 1-acetoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane, XII ($R = \text{Ac}$), which ought to result by acetolysis of XVII. It has now been found that XII ($R = \text{Ac}$) cannot be isolated by a slow acetolysis at 25° C., but a rapid reaction (five minutes) at 85° C. yields 47% of the expected yield of this compound from XVII in addition to a 28% yield of XX. This behavior is analogous with the acetolysis of methylene-bis-3,6-dinitro-1,3,6-triazacycloheptane (10) to 1-aceto-3,6-dinitro-1,3,6-triazacycloheptane and 1-acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane.

Confirmation for the structure of XII ($R = \text{Ac}$) was afforded by its conversion to the known 1-ethoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (5) by boiling in ethanol and by its nitrolysis either to 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazahexane with acetic anhydride and nitric acid or to RDX with nitric acid, acetic anhydride, and ammonium nitrate. These results are comparable with those obtained by the nitrolytic scission of XVII (at F and G) which yielded RDX and 1,7-diacetoxy-2,4,6-triazahexane with acetic anhydride and nitric acid, but only RDX when ammonium nitrate was included in the nitrolysis reagent.

The weakness of the bonds at G relative to those at F is indicated by the thermal decomposition of XVII to 1,5-dinitro-3,7-*endomethylene*-1,3,5,7-tetrazacyclooctane (DPT). This can be illustrated as passing through the intermediate XVIII formed by initial scission at G,G'. Subsequent loss of the elements of methylenenitrimine,* followed by recombination, would produce DPT.

The behavior of compounds XII and XVII indicates that the bond strengths at F and G must both have low values relative to the other linkages in this type of compound. Under these circumstances it might be expected that compounds such as VIII, X, XI, and XII would not be isolable from the nitrolysis of hexamine. The chemical reactions of XII and XVII show analogously that the type of product which terminates the reaction sequence VIII \rightarrow XII inclusive will depend on the decrease in stability of linkage F relative to that of the normally weaker bond at G. This decrease in stability will

* No evidence has ever been forthcoming to indicate that methylenenitrimine can cyclize to form Cyclonite. In the present instance no Cyclonite could be detected after the crude DPT was destroyed with hot 70% nitric acid.

produce Cyclonite rather than any one of the linear products and seems to be brought about by ammonium nitrate, which acts to prevent esterification during the reaction sequence VIII \longrightarrow XII.

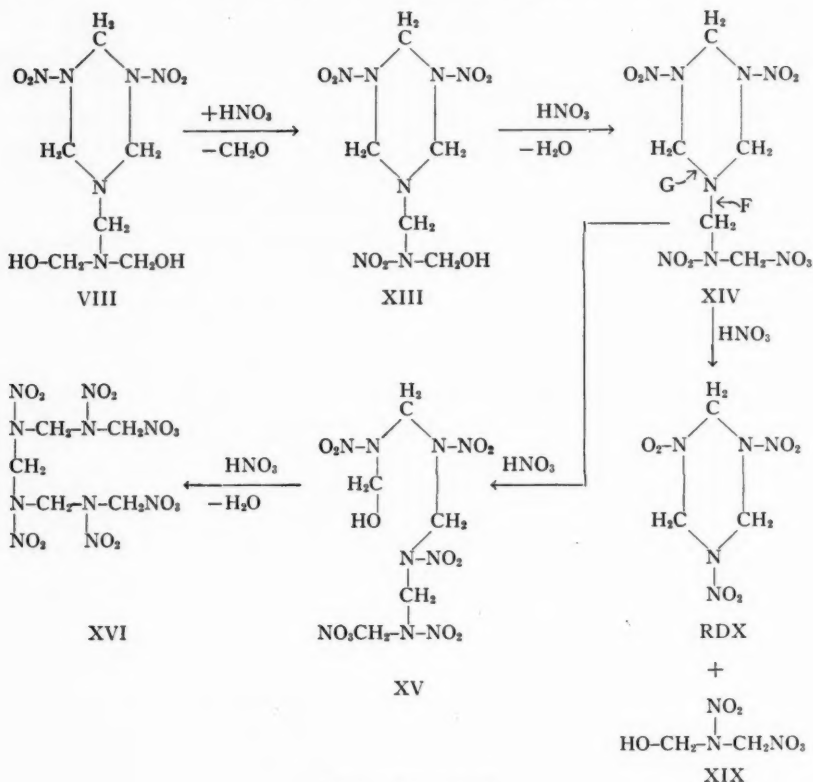
It is not to be expected that the reaction follows rigorously the indicated courses. Firstly esterification is known to occur in presence of anhydrous acids as an equilibrium reaction. Secondly esterification can be a slow process, and a competing reaction such as nitrolysis can overtake it. Indeed the yields which are obtained do not justify this mechanism as absolute, but only as preponderant.

Evidence for the simultaneous occurrence of pure nitrolysis and nitrolysis-esterification has been found in connection with the so-called anhydride processes for preparation of Cyclonite (2, 12). The course of both these methods can be considered, in the principal stage, as the reaction path HADN \longrightarrow VIII \longrightarrow RDX just outlined. Although an esterifying medium (acetic anhydride) is used, it is best maintained in proportionate minimal amount and the presence of ammonium nitrate undoubtedly promotes the demethylation-nitrolysis phases. The main product is certainly Cyclonite. Nevertheless we have been able to isolate from the Bachmann reaction mixture (89% RDX + HMX yield) a 3% yield of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane III and a 1% yield of diacetoxydimethylnitramide VII (6). From the Schiessler-Ross reaction mixture, these yields were 3% of III and 4.5% of VII.

One is tempted to draw a similar conclusion from an observation connected with the Hale hexamine nitrolysis where anhydride is, ostensibly, not involved. If the crude Cyclonite from such a nitrolysis is boiled in ethanol and the resulting solid is fractionally crystallized, a small amount of 1,9-diethoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane can be isolated. This is indicative of a slight esterification reaction to produce the 1,9-dinitroxy analogue, XVI. Its formation may be outlined as shown on p. 510.

According to this scheme, VIII first undergoes nitrolysis-demethylation, but esterification of the product XIII occurs before a second demethylation can occur. The resulting XIV can either nitrolyze at F to give Cyclonite (RDX) and hydroxy-nitroxydimethylnitramide, XIX, or it may nitrolyze at G to give XV which is then esterified to give XVI.

This latter mechanism is offered chiefly as an illustration of the complexity of the nitrolysis of hexamine rather than definitely to specify the mode by which XVI is formed. It must be recalled that compound XVI is produced in good yield by nitrolysis of DPT (9). The demonstrated presence of tetranitrotetrazacyclooctane, HMX, (4) in Hale Cyclonite indicates ephemeral presence of DPT. The trace of XVI which evidently is present in Hale Cyclonite could therefore have been formed by several alternative routes.



Experimental*

1,7-Dimethoxy-2,4,6-trinitro-2,4,6-triazaheptane, II

A. From Hexamine

To a stirred solution maintained at 15° C. of 60 gm. (0.556 mole of nitrogen pentoxide in 107 gm. (1.68 moles) of 99.8% nitric acid (titer, 106% HNO_3)) was added 20 gm. of hexamine (0.143 mole) over a 35 min. period. After 30 min. longer at 28° C. the mixture was poured into ice to precipitate a plastic mass. The aqueous diluate was neutralized with ammonia to yield 0.5 gm. of DPT, m.p. 187° to 200° C.

The plastic mass was unstable, so was immediately triturated with 300 cc. methanol in four portions. The Cyclonite was filtered off and the filtrate boiled down to one-quarter volume to yield, on filtration, a second crop of this substance, total weight 14.1 gm. or 44.5% of theoretical. The remaining methanol filtrate was poured into water to yield a semisolid oil which was extracted with 15 cc. carbon tetrachloride. The carbon tetrachloride slurry after one day was filtered. The solid was re-eluted with carbon tetrachloride.

* All melting points have been corrected against reliable standards.

finally to leave 13.2 gm. of product, m.p. 70° to 103° C. This material was separated by water-ethanol crystallization into 9.3 gm., m.p. 100° to 104° C. and a remainder m.p. 60° to 70° C. The latter was not further investigated. It ought to contain dimethoxydimethylnitramide.

The less water-ethanol soluble 9.3 portion (22% yield, 1 : 1 basis) contained some residual Cyclonite from which it was freed by repeated crystallization from water-ethanol, then benzene-petroleum ether (b.p. 60° to 70° C.) and finally from carbon tetrachloride. It then melted at 104° to 105° C. Calc. for $C_6H_{14}N_6O_8$: C, 24.2; H, 4.62; N, 28.3%. Found: C, 24.3; H, 4.63; N, 28.5%.

The molecular weight (Rast) was 276 to 291 (calc. 298) in camphor. The compound is soluble in acetone and benzene, moderately soluble in dioxane, methanol, and ethanol. It is difficultly soluble in petroleum ether (60° to 70° C.), ethyl ether, carbon tetrachloride, and water, and is best crystallized from the latter two solvents. It is slowly decomposed by hot ammonia and hot alkali. Its nitramine linkages are attested by decomposition in concentrated sulphuric acid and by a positive Franchimont test. Decomposition by the Kjeldahl method gives 13.1 to 13.3% nitrogen (Cyclonite gives 9.4 to 9.8%) while distillation from 30% alkali gives 5.3 to 5.4% basic nitrogen in the distillate.

When the nitrolysis procedure was altered by addition of the nitrogen pentoxide *after* the addition of hexamine, the results were radically different. A normal 82% yield (26.4 gm.) of Cyclonite was obtained and only 0.85 gm. of the 1,7-dimethoxy-2,4,6-trinitro-2,4,6-triazaheptane. Furthermore the yield of DPT obtained on neutralization of the aqueous filtrate was normal (3.13 gm.) at 10% of theoretical (1 : 1 basis).

B. From 1,7-Dinitroxy-2,4,6-trinitro-2,4,6-triazaheptane, IV

A suspension of 0.1 gm. (2.8×10^{-4} mole) of IV in 3 cc. of absolute methanol dissolved during five minutes' boiling. The solvent was evaporated to a small volume and the remainder was crystallized from aqueous ethanol (1 : 2.3) to melt at 103° to 104° C. with 60% recovery. Its mixed melting point with the material from hexamine was not lowered.

1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, III

A. From 1,7-Dimethoxy-2,4,6-trinitro-2,4,6-triazaheptane

A solution of 0.03 gm. (1×10^{-4} mole) of II in 0.33 cc. (8×10^{-3} mole) of 99% nitric acid and 0.5 cc. (5×10^{-3} mole) of acetic anhydride was heated 30 min. at 70° C. with some evolution of brown fume. After precipitation with ice and water, the crude III was filtered by suction (wt. 30 mgm., 84% of theory) and its melting point 148° to 149.5° C. was raised to 155° to 156° C. by crystallization from ethanol-water and then from carbon tetrachloride with 70% loss. A mixed melting point with material prepared according to Bachmann (3) was not lowered. Calc. for $C_8H_{14}N_6O_{10}$: C, 27.2; H, 3.96; N, 23.8%. Found: C, 27.3; H, 3.74; N, 23.8%.

B. From 1,7-Nitroxy-2,4,6-trinitro-2,4,6-triazaheptane, IV

A solution of 0.06 gm. (1.66×10^{-4} mole) of IV and 0.05 gm. (7×10^{-4} mole) of sodium acetate in 1 cc. of acetic acid was boiled for three minutes. Crystallization was effected after cooling by addition of 10 volumes of water. The precipitate (0.045 gm., 76% yield) melted at 154° to 155° C.; mixed melting point with material from the previous preparation was not lowered.

C. From 1-Acetoxy-7-ethoxy-2,4,6-trinitro-2,4,6-triazaheptane, V

After a solution of 0.66 cc. (0.016 mole) of 99% nitric acid and 1.02 cc. (0.01 mole) of acetic anhydride had been heated to 70° C., 60 mgm. (0.17×10^{-3} mole) of V was mixed in. After 30 min. at this temperature (nitrogen oxide evolution) the whole was poured into ice and water. The impure solid (m.p. 134° to 137° C., 88% if it had been pure) was repeatedly crystallized from acetone to melt at 154° to 155° C. A mixed melting point with material by methods A and B was not lowered.

D. From Hexamine

Acetic anhydride, 120 cc. (1.22 mole), was placed in a flask and maintained at 20° C. with an ice bath while 44 cc. (1 mole) of 99% nitric acid was added to it with stirring. To this solution was added a solution of 33.6 gm. (0.24 mole) of hexamine in 55 cc. (0.97 mole) of acetic acid over a period of 30 min. at 15° to 20° C. The suspension was then warmed to 75° C. and cooled to 15° C. while 40 gm. (0.5 mole) of 50% aqueous sodium hydroxide was added dropwise with cooling. The reaction mixture was then cooled to 5° C. and the precipitate filtered off and washed with 100 cc. of acetic acid. Weight of crude III was 50.8 gm., m.p. 133° to 135° C. Yield calculated as crude is 60% of theory (1 : 1 mole basis). This can be purified further by crystallizing from acetic acid whereby the yield of almost pure diacetoxynitrotriazaheptane is 51% of theory, m.p. 153.5° to 154° C.

The reaction filtrate and the acetic acid washings, to which 100 cc. of acetic anhydride was added to keep the solution anhydrous, were concentrated by distilling off the acetic acid under reduced pressure. The residue obtained in this way was extracted with ether and found to contain 19.1 gm. of almost pure diacetoxymethylnitramide (VII), b.p. 151° to 160° C. at 12 to 13 mm. pressure. The refractive index of this liquid was 1.4527 at 25° C. (6). Yield calculated on the basis of 1 mole of hexamine giving 1 mole of VII was 39% of theory.

There seemed to be some loss of VII owing to decomposition during the distillation, and the final yield obtained did not therefore represent the total amount of VII formed in the reaction.

E. From 1-Acetoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane, XII

A solution of 1.05 ml. (0.025 mole) of 99% nitric acid in 5 ml. (0.05 mole) of acetic anhydride was treated at 25° C. with 1.25 gm. (0.005 mole) of XII. The warm solution was further heated to 50° C. for one-half hour, then cooled, diluted, and filtered to yield 1.65 gm., m.p. 144° to 148° C. Crystallization

from hot acetic acid yielded 1.43 gm., m.p. 152.5° to 154° C. Since a mixed melting point with III prepared otherwise was not lower, the yield is 81% of theoretical. No RDX was detectable after destruction of the product with hot 70% nitric acid.

1-Acetoxy-7-ethoxy-2,4,6-trinitro-2,4,6-triazaheptane, V

As an alternative variation of the RDX preparations, hexamine was treated with nitric acid and acetic anhydride at -25° C. A solution was prepared at -25° C. by slow addition of 306 gm. (4.86 moles) of 99 to 100% nitric acid to 222 gm. (2.15 moles) of acetic anhydride. To this stirred solution at -25° C. was added 20 gm. (0.143 mole) of hexamine over a 90 min. period. The reaction mixture contained white solid. After an additional 30 min. the mixture was poured into 1600 gm. of ice and water. The precipitate was filtered and washed neutral to bromcresol green paper. The vacuum dried weight was 30.5 gm., m.p. 135° to 138° C.

Oxidation of this crude product with hot 70% nitric acid showed that it contained 24% of RDX, m.p. 203° to 204° C., a yield of 7.3 gm. or 23% of theoretical. Twenty grams of the crude product was extracted thrice with 60 cc. portions of boiling 95% ethanol to give 8.6 gm. of material, m.p. 95° to 110° C., but not clear until 130° C. The estimated yield at this point was 15%. This material was crystallized eight times from either ethanol-water, benzene-petroleum ether (60° to 70° C.) or carbon tetrachloride until a constant melting point of 106° to 107° C. was obtained. Complete destruction of this material with hot 70% nitric acid showed that no RDX was present. After hydrolysis with alkali it gave a positive acetate test with lanthanum nitrate. The compound gave a positive Franchimont nitramine test. Calc. for $C_8H_{16}N_6O_9$: C, 28.5; H, 4.71; N, 24.7; CH_3CO , 12.7%. Found: C, 28.3; H, 4.76; N, 24.9; CH_3CO , 13.4%.

The compound gave a positive nitramine test and reduction with sodium amalgam gave a salicylaldehyde spot test for hydrazine (Feigl). Hydrolysis with dilute sulphuric acid gave no hydroxylamine. The compound decomposed in boiling 6% hydrochloric acid after 30 min. to give no water insoluble residue. The solution thus obtained from 0.3435 gm. in 8.5 cc. of 6% hydrochloric acid gave duplicate yields of formaldehyde-dimedone derivative (7) which checked within 0.5% and corresponded to 0.1144 gm. formaldehyde. This represents 13%, or half, of the carbon in the original sample.

1,7-Dinitroxy-2,4,6-trinitro-2,4,6-triazaheptane, IV

A. From 1-Acetoxy-7-ethoxy-2,4,6-trinitro-2,4,6-triazaheptane, V

To 0.6 cc. of 99% nitric acid at 0° C. was added 80 mgm. (2.4×10^{-4} mole) of V. After warming to 20° C. over 20 min. and then drowning in water a 65 mgm. yield was obtained of material, m.p. 145° to 146° C., (crude yield 77%). This was crystallized from 1:1 dioxane-carbon tetrachloride to melt at 153° to 154° C. (35% pure yield).

B. From 1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, III

After 1.00 gm. (2.8×10^{-3} mole) of III was added to 8 cc. (0.19 mole) of 99% nitric acid at 0° C., the clear solution after one hour at 20° C., was drowned in 12 volumes of ice and water. The crude precipitate (91% of theoretical) was dissolved in 8 cc. dioxane at 20° C. and 8 cc. of carbon tetrachloride was added at once. The crystals melted at 151.5° to 152° C. (0.55 gm. or 54% of theoretical). Two subsequent crystallizations raised the melting point to 154° C. (decomp.) when inserted into the rising bath at 148° C. Mixed melting point with product from preparation A was not lowered but with III it was lowered to 147° C. (insertion at 146° C.). The material is a powerful explosive very sensitive to impact when pure. Calc. for $C_4H_8N_8O_{12}$: C, 13.3; H, 2.24; N, 31.2%. Found: C, 13.7; H, 2.33; N, 31.6%.

The compound is destroyed by prolonged contact with water.

1,7-Diethoxy-2,4,6-trinitro-2,4,6-triazaheptane, VI

A suspension of 0.17 gm. (4.7×10^{-4} mole) of IV in 4 cc. of 99% ethanol was refluxed for 25 min. Dilution with 10 cc. water precipitated 80 mgm. 52.2% of theoretical of product, m.p. 79° to 80.5° C. Two crystallizations from aqueous ethanol (1 : 2.3) did not raise the melting point. Calc. for $C_8H_{18}N_6O_8$: C, 29.4; H, 5.58; N, 25.8%. Found: C, 29.6; H, 5.60; N, 26.1%.

1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, III

A. From Schiessler-Ross Synthesis of Cyclonite

To a solution of 57 cc. (1.0 mole) of acetic acid in 246 cc. (2.6 moles) of acetic anhydride at 70° C. was added with stirring, simultaneously and equivalently, a mixture of 80 gm. (1 mole) of ammonium nitrate and 30 gm. (1 mole) of Roessler and Hasslacher paraform over a period of 25 min. The temperature during the addition was maintained at $70^\circ \pm 2^\circ$ with slight cooling required. The reaction mixture was stirred 20 min. longer at 65° to 70° C., cooled to 35° C., diluted with 300 cc. water, cooled to 10° C., and filtered. Weight of product was 38.6 gm., m.p. 196° to 198° C. (shrinkage 195° C.). Yield calculated as crude Cyclonite was 52.3% of theory (formaldehyde basis). This was found to contain 89% of pure RDX-HMX on "fume off" with 70% nitric acid.

Although the crude Cyclonite contained some III, only the products in the acid filtrate were examined. The acetic acid filtrate was neutralized to pH 6 with 28% aqueous ammonia and the water distilled off under reduced pressure. The residue from the distillation was allowed to cool until it had completely solidified. The water insoluble products were removed by swirling the solid cake in water and filtering off the undissolved material. This gummy solid was dissolved in 25 cc. of acetone and the solvent then evaporated almost to dryness under a stream of air. The solid product obtained in this manner was not sticky; weight was 5.07 gm. It was separated by crystallization from acetone, ethanol, ethyl acetate, acetic acid, and water into the

following product; quantities are based on per cent of theoretical on the formaldehyde basis:

1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane	2.1%
1-Aceto-3,5-dinitro-1,3,5-triazacyclohexane	1.1%
1-Aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane	2.8%
Cyclonite and HMX	traces

B. From Bachmann Synthesis of Cyclonite

The synthesis of Cyclonite by this method is described below. Essentially the same separation as that outlined above gave a 3% yield of III and only traces of the other compounds.

Diacetoxymethylnitramide, VII, from Anhydride Processes

A. From Schiessler-Ross Synthesis of Cyclonite

To a solution of 228 cc. (4 moles) of acetic acid in 984 cc. (10.4 moles) of acetic anhydride were added at 70° C. with stirring, a finely ground mixture of 120 gm. (4 moles) of Roessler and Hasslacher paraform and 320 gm. (4 moles) of ammonium nitrate over a period of 27 min. The reaction mixture was stirred 20 min. longer at 70° C., cooled to 15° C., and 240 gm. (3 moles) of 50% aqueous sodium hydroxide was added dropwise while the temperature was held below 20° C. The heavy sludge thus formed was cooled to 0° C. and filtered. The filter cake was washed with 200 cc. of acetic acid which was added to the acid filtrate. The weight of this precipitate was 146 gm., m.p. 184° to 188° C.; yield calculated as crude RDX-HMX is 50% of theory (formaldehyde basis).

The acid filtrate was concentrated by distilling off the acetic acid at 11 mm. pressure. The sludge which remained was extracted with three 400 cc. portions of ether. The ether extracts were concentrated under a pressure of 12 mm. to an oily residue which was suspended in 250 cc. water and the resulting sticky emulsion was neutralized to pH 8 with sodium carbonate and then extracted again with five 150 cc. portions of ether. The ether extracts were dried over sodium sulphate. The ether was removed by distillation under reduced pressure. A yellow oil remained which was distilled by flash distillation at a pressure of 12 mm. This method was used since the oil was contaminated with other products which decomposed violently when all the material was distilled at one time. In distilling, the oil was added dropwise from a separatory funnel to a 25 cc. Claisen flask which was immersed in an oil bath at 200° to 215° C. A pressure of 12 mm. was maintained in the system by regulating the addition of the oil. Each drop was allowed to distill over before the next drop was added in order to avoid an explosion. The distillate collected in this way smelled strongly of formaldehyde owing to decomposition during the distillation, so it was suspended in 60 cc. of water and neutralized to pH 7.5 to 8 with sodium carbonate and again extracted from the water with three 40 cc. portions of ether. The ether extracts were dried over sodium sulphate, then the solvent was removed and the oily residue

distilled at 12 mm. The fraction boiling at 153° to 156° C. at 12 mm. (weight 6.0 gm.) was almost pure diacetoxydimethylnitramide (VII). It was identified as such by analysis (elemental), refractive index, and by nitration with 99% nitric acid whereupon it gave a 38% yield of dinitroxydimethylnitramide, identified by mixed melting point with an authentic sample. The crude yield of VII was 2.4% of theory (formaldehyde basis) while the yield of pure material, b.p. 153° to 156° C. at 12 mm. was 1.5%.

B. From Bachmann Synthesis of Cyclonite

A Bachmann Cyclonite reaction, rich in acetic anhydride, was carried out by adding a solution of 33.6 gm. (0.24 mole) of hexamine in 160 cc. (2.8 moles) of acetic acid and a solution of 38.4 gm. (0.48 mole) of ammonium nitrate in 41 cc. (0.96 mole) of 99% nitric acid, simultaneously to 226 cc. (2.4 moles) of acetic anhydride at $69^{\circ} \pm 1^{\circ}$ over a period of 22 min. Throughout the addition a 90 sec. lead of nitric acid : ammonium nitrate was maintained. The suspension was stirred 15 min. longer after the addition at 70° C., then cooled to 20° C. and 30 gm. (0.37 mole) of a 50% aqueous sodium hydroxide solution was added, keeping the temperature below 20° C. The resulting slurry was cooled to 5° C. and the precipitate filtered, washed with 150 cc. of acetic acid, and dried at 50° C. Weight of Cyclonite was 66.5 gm., m.p. 187° to 192° C. The acid filtrate, together with the acetic acid washings, was concentrated under reduced pressure and the diacetoxydimethylnitramide was isolated as in the Ross reaction (described above). A further 7.6 gm. of crude Cyclonite was obtained during the working up of the filtrate. The total crude yield of Cyclonite was then 74% of theory (2 : 1 mole basis). The yield of relatively pure VII obtained was 0.5 gm., b.p. 150° to 155° C. at 11 mm. The refractive index at 25° C. was 1.4526. Yield is 1.0% on basis of 1 mole of hexamine giving 1 mole of VII.

When the usual Bachmann reaction was carried out where the hexamine : nitric acid : ammonium nitrate : acetic acid : acetic anhydride molar ratio was 1 : 4.18 : 2.54 : 11.6 : 7.1, a 0.9% yield of crude VII was obtained, b.p. 147° to 160° C. at 12 mm.

Methylene-bis-1-[3,5-dinitro-1,3,5-triazacyclohexane]

A ground suspension of 24 gm. (0.1 mole) of 3,5-dinitro-3,5-diazapiperidinium nitrate (13) in 60 cc. acetone was maintained at 5° to 7° C. and stirred while 0.1 mole (60 cc.) of 6.6% aqueous sodium hydroxide was added over 25 min. The pH did not exceed 5.6. The mixture was then filtered to yield a precipitate which weighed 9.3 gm. after fivefold washing with cold water, twofold washing with ethanol, and finally with ether. This crude yield, melting at 130.5° to 131° C. was, then, 50.7% of theoretical. Any contaminating RDX could be removed by centrifugation of this crude material, finely ground, in an ethylene dibromide - petroleum ether (b.p. 90° to 100° C.) mixture of density 1.71 to 1.72. The portion less dense than this medium was dissolved in 70 cc. nitromethane, filtered, and the filtrate treated with 140 cc. of dry ether. This yielded 7.1 gm., m.p. 132.6° to 132.8° C. of

pure material, or 39% of theoretical. The product yielded no Cyclonite after digesting with hot 70% nitric acid. An alternative purification involved solution in 200 cc. acetone with subsequent crystallization after dilution with 100 cc. of petroleum ether (b.p. 40° to 60° C.). Calc. for $C_7H_{14}N_{10}O_8$: C, 22.95; H, 3.83; N, 38.3%. Found: C, 23.18; H, 4.25; N, 38.5%. The 10% discrepancy in the hydrogen value is typical of all results from the analysts (Arlington Laboratories) on all compounds containing the methylenenitramine linkage. The error may be minimized by slow burning of the sample and by admixture with potassium dichromate.

This compound was converted to 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane (4) in 49% yield (1 : 1 basis) when 0.105 gm. (2.9×10^{-4} mole) was dissolved in 1 cc. of acetic anhydride over 15 min. shaking. After 10 hours the solution was diluted with water, filtered after long hydrolysis, and neutralized to pH 6.5 with aqueous alkali. The precipitate weighed 30 mgm. and melted at 145° to 148° C. Crystallization from ethanol raised this melting point to 153° to 155° C., and a mixed melting point with an authentic sample was not lowered. Omission of the long period of hydrolysis lowered the yield markedly because of unworkable impurities.

1-Acetoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane, XII

Acetolysis of XVII at room temperature over a long period of time caused by-product formation which obscured the principal reaction products. This by-product formation was minimized by addition at once of 25 gm. (0.0683 mole) of methylene-bis-dinitrotriazacyclohexane to 65 cc. (0.69 mole) of acetic anhydride and 80 cc. of acetic acid at 65° to 75° C. Solution was complete after two minutes. The temperature was maintained at 85° C. for four to six minutes and then lowered to -40° C. and allowed to warm slowly to 5° C. The crystalline precipitate was filtered and washed with petroleum ether (b.p. 60° to 80° C.). The product, m.p. 101° to 137° C., weighed 10.2 gm. or 60% of the expected yield of acetoxymethyldinitrotriazacyclohexane, XII. It was purified by solution in 70 cc. dry acetone from which it was precipitated by 80 cc. dry petroleum ether (b.p. 60° to 80° C.). Filtration at 0° C. yielded 8.0 gm. (47% of theory), m.p. 141° to 143° C. Repeated crystallization

XII. INTERPLANAR SPACING, Cu-K α RADIATION

<i>d</i> , kX	Relative intensity 1-10	<i>d</i> , kX	Relative intensity 1-10	<i>d</i> , kX	Relative intensity 1-10
9.05	9	3.30	6	2.43	3
6.64	8	3.15	9	2.37	3
6.05	8	3.04	7	2.32	4
5.63	10	2.92	4	2.25	1
5.06	8	2.83	2	2.17	1
4.54	7	2.77	4	2.06	1
4.20	7	2.67	1	1.99	1
3.91	7	2.59	8	1.95	1
3.57	9	2.53	2		

raised this melting point to 143.7° to 144.7° C. Calc. for $C_6H_{11}N_5O_6$: C, 28.9; H, 4.45; N, 28.1; CH_3CO , 17.3%. Found: C, 29.1; H, 4.39; N, 28.5; CH_3CO , 17.6%.

The filtrate from which XII was isolated was vacuum evaporated to dryness and the residue extracted with acetone at 25° C. to leave 6.8 gm. of an intractable, white material, m.p. 144° C. Evaporation of the acetone left a syrup from which 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, XX, m.p. 156° to 157° C., was obtained by five minutes boiling with water. Yield was 4.2 gm. or 28% of theoretical.

When 0.5 gm. (0.002 mole) of 1-acetoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane was dissolved in 4 cc. absolute ethanol over five minutes, the cooled solution yielded 0.17 gm. (36% of theory) of 1-ethoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (m.p. 110° to 111° C.). Purification from boiling ethyl ether raised the melting point to 114° to 117° C., dependent on rate of heating.

Conversion of acetoxymethyldinitrotriazacyclohexane, XII, to Cyclonite in 73% yield was effected by proportionate addition of 1.25 gm. (0.005 mole) of this compound and a solution of 0.26 gm. (0.0032 mole) of ammonium nitrate in 0.27 ml. (0.0065 mole) of nitric acid over 35 min. to 2.7 ml. (0.027 mole) of acetic anhydride and 1 ml. of acetic acid at 67° to 71° C. Initial addition of the solid was retarded 5% behind that of the nitric acid solution. Subsequent dilution by 75 ml. of cold water precipitated 1.08 gm., m.p. 139° to 196° C. When this crude product was boiled with 70% nitric acid, recovery of Cyclonite, m.p. 200° to 203° C. (softening at 197° C.) was 0.81 gm. Identity was authenticated by mixed melting point.

Nitrolysis of Methylene-bis-dinitrotriazacyclohexane

If 0.105 gm. (2.9×10^{-4} mole) of methylene-bis-dinitrotriazacyclohexane was suspended in 0.2 ml. (2×10^{-3} mole) of acetic anhydride plus 0.04 ml. (10^{-3} mole) of 98% nitric acid and warmed to 35° to 40° C., then chilled and maintained at 28° C. for one hour, a 35% yield of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane was obtained and identified by mixed melting point. Isolation involved drowning of the mixture in water. The precipitate was filtered off (m.p. 130° to 135° C., weight 0.13 gm.) and dissolved in hot acetic acid. The crystal crop of 0.05 gm. (78% of theoretical 1:1 basis) of Cyclonite, m.p. 200° to 202° C., was filtered off and identified by mixed melting point. Dilution of the warmed filtrate with ether yielded 0.035 gm. of diacetoxyltrinitrotriazazaheptane.

When equimolar quantities of methylene-bis-dinitrotriazacyclohexane and benzoyl nitrate (7) in dry acetone at -5° C. were allowed to react for 30 min. a product melting at 115° to 136° C. was obtained, which could partially be purified to melting point 147° to 148° C. by wash with acetone. This has not been identified. Partial destruction of the evaporated filtrate by 70% nitric acid left a 33% yield (mole for mole) of RDX.

1,9-Diethoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane from Crude Hale Cyclonite

When the dry crude Hale product (wt. 356 gm., m.p. 200° to 203.5° C. with shrinkage at 194° C.) from 2 moles hexamine and 40 moles 99% nitric acid was refluxed with boiling absolute ethanol for eight hours, the suspended RDX which was then filtered off melted at 203° to 203.5° C. (shrinkage 200° C.). The ethanolic filtrate was fractionally evaporated, and the content alternately crystallized fractionally 20 times from ethanol, dioxane, toluene, carbon tetrachloride, and mixtures of these. There were thus separated impure Cyclonite, impure 3,5-dinitro-3,5-diaza-1-oxacyclohexane and 5 mgm. of pure 1,9-diethoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane, m.p. 166° to 167° C. (mixed melting point not lowered). This result should, of course be considered qualitatively.

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NITROLYSIS OF HEXAMETHYLENETETRAMINE

VI. RECOMBINATION OF FRAGMENTS DURING HEXAMETHYLENE-TETRAMINE NITROLYSIS IN ACETIC ANHYDRIDE¹

By E. ARISTOFF, J. A. GRAHAM, R. H. MEEN, G. S. MYERS, AND
G. F. WRIGHT

Abstract

Alternative hypotheses can account for the yield of more than one equivalent of Cyclonite from hexamine when the Bachmann reagents, ammonium nitrate, nitric acid, and acetic anhydride are used. In the nitrolysis, evidence for a stepwise synthesis from unit fragments is presented as the enhanced yield when methylenedinitramine is added with paraform to ammonium nitrate and acetic anhydride according to the Schiessler-Ross method for Cyclonite synthesis. However, this evidence is discounted because the expected by-product, 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane is not found. Alternatively it is believed that the Bachmann reaction is actually a combination of the direct nitrolysis of hexamine with nitric acid, concurrent with a resynthesis of hexamine from the fragments produced by the nitrolysis. On this basis all by-products from the hexamethylenetetramine nitrolysis must be accounted as degradation products of hexamethylenetetramine and not capable of synthesis from unit fragments like formaldehyde, ammonia, and acetic acid. No exception has been found; the addition of acylamides to the Bachmann reaction mixture increases the yield of two by-products, 1-acyl-3,5-dinitro-1,3,5-triazacyclohexane and 1-acyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane. It has been shown that these can be formed only from degradation products of hexamethylenetetramine such as 1,5-diaceto-3,7-endomethylene-1,3,5,7-tetrazacyclooctane and acetaminomethylhexamethylenetetramine nitrate.

When ammonium nitrate is used together with nitric acid for the nitrolysis of hexamine in acetic anhydride, yields of Cyclonite are obtained which are greater than might be expected if one mole of hexamine were converted to one mole of the explosive (2). This process therefore differs from the Hale method by which hexamine is nitrolyzed in nitric acid alone. Yields from the latter reaction are always less than 100% on the 1 : 1 molar basis (13). It also differs from the Ross-Schiessler process which employs formaldehyde and ammonium nitrate in acetic anhydride and gives yields of 50 to 60% on the formaldehyde basis (18). The name that Bachmann has applied to his method (The Combination Process) implies that it includes both the Hale and the Ross-Schiessler reactions.

According to this implication, hexamine first reacts with the nitric acid to form Cyclonite and fragments involving formaldehyde. These fragments have to recombine in some manner to provide a cyclic structure from which more Cyclonite can be formed. The recombination would, according to this reasoning, take place by the reaction through which Ross and Schiessler obtained Cyclonite.

¹ Manuscript received November 16, 1948.

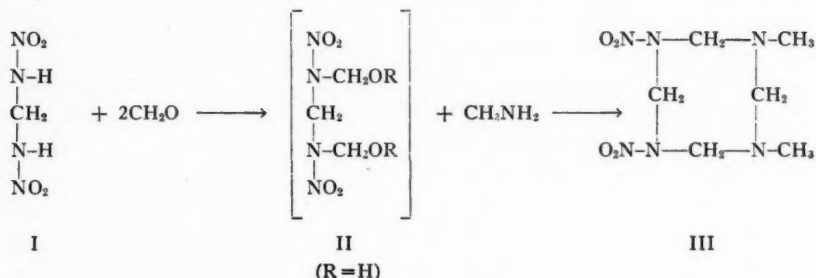
Contribution from the Chemical Laboratory, University of Toronto, Toronto, Ontario.

In order to establish this scheme for Bachmann's synthesis, the method by which the Ross-Schiessler reagents combine must be known. There are two alternatives. Firstly, simple or polymeric methylenenitramine units might be formed and then cyclize to produce Cyclonite. In this event, the Hale nitrolysis might not be involved at all in the Bachmann process; the latter, too, could involve cyclization of methylenenitramine units. The second alternative would involve combination of the fragments of formaldehyde and ammonia to form hexamine (or a compound of similar complexity) which could then be degraded to Cyclonite by the path suggested for the Hale reaction (8, 16).

Either of these alternatives enjoys a certain amount of experimental evidence which seems to support it. Some of this evidence will be presented in the present report. It will be evaluated largely on the basis that any mechanism which is postulated must not only explain the formation of the principal product (Cyclonite) but also the by-products which are obtained at the same time. When the evidence presented thus far in this series, "Nitrolysis of Hexamine", has been so evaluated, it has indicated that neither Cyclonite nor a by-product has arisen in the nitrolysis medium by direct synthesis from smaller units but always by degradation of a larger unit.

The following experiment would indicate that Cyclonite can be formed from a linear methylenenitramine unit. The yield of Cyclonite in the Schiessler-Ross process is relatively low compared with that obtained by the Bachmann method, and maximum yields of 58 to 64% are the highest attainable by the former method. If in a Schiessler-Ross reaction mixture (1 mole of paraform, 1.25 moles of ammonium nitrate, and 10 moles of acetic anhydride) one includes one-fifth mole of methylenedinitramine, the crude Cyclonite yield is raised to 81% of theoretical. If two-fifths mole of methylenedinitramine is employed, the yield is increased to 87%. These yield increases cannot be owing to the formaldehyde which might be contributed by decomposition of the methylenedinitramine for several reasons. First, the amount contributed by decomposition would be insufficient in quantity. Second, a duplicate experiment wherein one-fifth mole of methylenedinitramine was used and the paraform was omitted gave a yield of only 10% of the Cyclonite which might be formed by this decomposition. A small amount of 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane (17) (II, R=Ac) was obtained as well, showing that the decomposition did occur.

Although the discoverers (5) of methylenedinitramine, I, and others (22) had characterized it adequately, we sought further confirmation of the identity of the material which we prepared by their method. While its reaction with formaldehyde and ammonia produced no definite product, two substances were obtained with formaldehyde and methylamine.



According to analyses, one of these compounds ought to be the cyclic 1,3-dinitro-5,7-dimethyl-1,3,5,7-tetrazacyclooctane, III. The other could not be identified. Its insolubility in acetone indicates that it is either a polymer or a salt. Both substances were thermally unstable.

This reaction typifies a strong tendency toward methylation of methylenedinitramine. Although we were unsuccessful in attempts to isolate the dimethylol derivative of II (R=H) (22), this methylation could be demonstrated by digestion of methylenedinitramine with formaldehyde, sodium acetate, and acetic anhydride at 95° C. A 9% yield of 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane, II (R=Ac), was obtained in addition to considerable amorphous polymeric material. One may assume, therefore, that 1,3-dihydroxy-2,4-dinitro-2,4-diazapentane, II (R=H), is reasonably stable in hot acetic anhydride.

The stability of II (R=Ac) was demonstrated by treating it with 98% nitric acid. A 22% yield of 1,5-dinitroxy-2,4-dinitro-2,4-diazapentane, II (R=NO₂), was obtained in this way and identified with that prepared from 3,5-dinitro-3,5-diaza-1-oxacyclohexane (17).

Although it can thus be shown that methylenedinitramine will enhance the yield in the Schiessler-Ross reaction, and also will methylolate in acidic media, it does not necessarily follow that it is an intermediate in the normal reaction carried out at 60° to 70° C. which yields over 50% of the theoretical amount of Cyclonite. Indeed there is evidence against its presence, since a careful search of the products of this reaction has failed to discover any 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane, II (R=Ac) (8). It will be recalled that this compound was isolated when methylenedinitramine deliberately was added to the otherwise normal Schiessler-Ross reaction.

On the other hand, II (R=Ac) can be isolated in 1.4% yield (ammonium nitrate basis) when the Schiessler-Ross reagents are stirred together at room temperature for 25 times the normal reaction period. The reaction could not, however, be considered normal since the Cyclonite yield was only about 5% of theoretical and much polymeric material was present. An 18% yield of 3,7-*endomethylene*-1,5-dinitro-1,3,5,7-tetrazacyclooctane (DPT) was obtained as well, thus indicating the presence of dimethylnitramide (6).

The situation with regard to methylenedinitramine can be summarized by the observation that it can be formed in a Schiessler-Ross reaction mixture, but not under conditions which are favorable to Cyclonite formation. Its significance in support of a reaction mechanism involving the direct construction of Cyclonite from small methylenenitramine units is therefore questionable.

The enhancement of Cyclonite yield when methylenedinitramine is added to the Schiessler-Ross reagents cannot be questioned, but the action of this substance can be explained otherwise than by direct participation in the formation of Cyclonite. Its strong tendency toward methylation may have the effect of withholding formaldehyde from the direct reaction until it is needed. Formaldehyde which is withheld in this manner will be less available for side reactions. One of the principal side reactions which prevents high yield in the Schiessler-Ross reaction is acetylation. Methylene diacetate will not form Cyclonite with acetic anhydride and ammonium nitrate.* It is suggested that the methylenedinitramine may be effective in reducing the tendency toward methylene diacetate formation.

The alternative to a synthesis of Cyclonite from methylenenitramine units is a synthesis of hexamine from formaldehyde and ammonium nitrate as part of the main reaction in the Schiessler-Ross process or as a secondary reaction in the Bachmann process. The nitration, according to this mechanism, will occur in the same manner as it does in the Hale process. Such a mechanism is inherently reasonable. Thus Baur and Ruetschi have shown that hexamine can be formed in acidic media (3) and Williams and Winkler have isolated it from formaldehyde and ammonium nitrate in acetic acid solution (21). Unfortunately hexamine reacts with acetic anhydride, so that these latter workers were unable to show its presence in a medium comparable with that employed by the Bachmann or Schiessler-Ross procedures, although they have postulated that its formation is necessary for Cyclonite formation in the latter procedure.

Direct proof is therefore lacking for a mechanism involving hexamine synthesis or resynthesis in these two anhydride processes. The indirect method which has been used successfully in this series, "Nitrolysis of Hexamine", has involved the isolation and identification of by-products, followed by a demonstration that they cannot be built up from smaller nitramine units, but must, instead, have been formed by degradation of hexamine. The remainder of this report will show that the by-products 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X, and 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, always occur together in every Bachmann and Schiessler-Ross reaction; further that they must have been formed by degradation of hexamine.

The ordinary reaction mixture contains about 3% of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, and about 1% of 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X, on the basis that one mole of each is derived from one

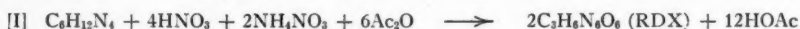
* We are indebted to Dr. Paul Olynik for an investigation which showed that no Cyclonite could be isolated in a preparation where methylenediacetate was used instead of paraform in the Schiessler-Ross reaction.

mole of hexamine. Both are obtained by neutralization of the reaction liquors after the main product, Cyclonite, is filtered off (8). They have been identified by quantitative elemental, ammonia, and formaldehyde analyses and by qualitative detection of acetic acid from the products of decomposition. They have been converted by absolute nitric acid into 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane, HMX, and Cyclonite, RDX, respectively.

The yields of both of these compounds can be increased (to 7.5% of the cyclooctane derivative VI) by use of a large excess of acetic anhydride in the Bachmann procedure (20). This suggests that the excess reacts with one of the ingredients: the nature of the by-product would indicate that acetamide is involved. Since both ammonium acetate and ammonium nitrate are present in the Bachmann reaction mixture, the action of acetic anhydride on each of these salts has been examined.

An 83% yield of acetamide was obtained when ammonium acetate was heated with the anhydride for a short time. The reaction with ammonium nitrate was much slower, but a yield of 7% of acetamide could be isolated; twice as much probably was present. When nitric acid was added to either of these reaction mixtures, no acetamide was formed.

Since nitric acid inhibits acetamide formation and yet is necessary for the subsequent nitrolysis there ought to be an optimum nitric acid - ammonium nitrate ratio for maximum yield of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, if its formation involves acetamide. Table I shows that this is the case when an excess of acetic anhydride is used over that required by Equation I.



and the ratio $\text{HNO}_3/\text{NH}_4\text{NO}_3$ is varied from 2 (as required by this equation) between the limits 1.5 and 2.5.

TABLE I

YIELD OF 1-ACETO-3,5,7-TRINITRO-1,3,5,7-TETRAZACYCLOOCTANE FROM BACHMANN TYPE REACTION USING 0.05 MOLE HEXAMINE AND 0.6 MOLE ACETIC ANHYDRIDE

Moles HNO_3 Moles NH_4NO_3	2.4	2.2	2.1	2.0	1.9	1.8	1.7	1.6	1.5
Yield, mgm.	20	23	1.5	145	400	460	310	230	200

If acetamide were necessary for the ultimate formation of acetotrinotetrazacyclooctane, VI, and acetodinitrotriazacyclohexane, X, then deliberate addition of such an acid amide to the reaction mixture ought to increase the yield of these aceto compounds. This was found to be the case when 1 mole each of acetamide and hexamine in acetic acid were added to 9 moles of acetic anhydride proportionately with a solution of 4 moles of nitric acid and 2.5 moles of ammonium nitrate. The presence of the acetamide not only lowered the yield of Cyclonite to 58% but it also caused the formation of at least 8.5%

of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, and 3.5% of 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X, expected if one mole of each was formed from one mole of hexamine.

One might question the significance of this acetamide addition in a medium consisting largely of acetic acid and anhydride. The significance was verified by use of propionamide rather than acetamide. After removal of a 39% yield of Cyclonite, the neutralized liquors precipitated an 8.5% yield of 1-propanoyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane. This compound was adequately identified by quantitative elemental analysis and by qualitative identification of the propanoic acid produced by its decomposition in sulphuric acid. Also the compound was converted by absolute nitric acid to 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane. It would seem, therefore, that the acid amide was a significant constituent, at least so far as the tetrazacyclooctane was concerned. We failed, however, in the synthesis of the corresponding benzoyl derivative when we included benzamide with the reagents used in the Bachmann process. A good yield of methylene-bis-benzamide was obtained instead.

It should not be implied that the acid amides were replacing ammonium nitrate in the process. Evidence that they were *supplementing* the nitrate salt was furnished by several experiments. When half the ammonium nitrate required by Equation I was replaced by acetamide the Cyclonite yield was reduced to 41% (2 : 1 basis) and the acetotrinitrotetrazacyclooctane yield to 5.3%. When all of the ammonium nitrate was replaced by acetamide only 22% of Cyclonite was obtained and none of the aceto compound, VI, could be detected. A 19% yield (1 : 1 basis) of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane appeared instead.

By analogy with the postulated formation of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) and Cyclonite (15, 16) one might expect that the aceto compounds found as by-products in the processes involving acetic anhydride would result from substances comprising acetamide, formaldehyde, and ammonia. Two known compounds appeared as possibilities since they both seemed to contain acetamino linkages. The first of these was a compound prepared by the action of one equivalent each of nitric acid and acetic anhydride on hexamine (14) and later designated as the quaternary salt (1) 1-acetamidomethylhexamine-1-nitrate, IV, by Bachmann and coworkers. The other possibility was a compound prepared from hexamine and acetic anhydride alone (10) by Dominikiewicz who specified it as diacetylpentamethylenetetramine. Neither compound was reported as preparable from acetamide, formaldehyde, and ammonia, and all attempts by us to prepare either from these reagents in acetic anhydride or acetic acid failed completely. It thus appeared that if these compounds turned out to be responsible for acetotrinitrotetrazacyclooctane, VI, and acetodinitrotriazacyclohexane, X, then they must have been secondary alterations of the true resynthesis product, hexamine.

When the first-mentioned of the two compounds, so-called 1-acetamidomethylhexamine-1 nitrate was treated with the Bachmann reagents at 65° C.

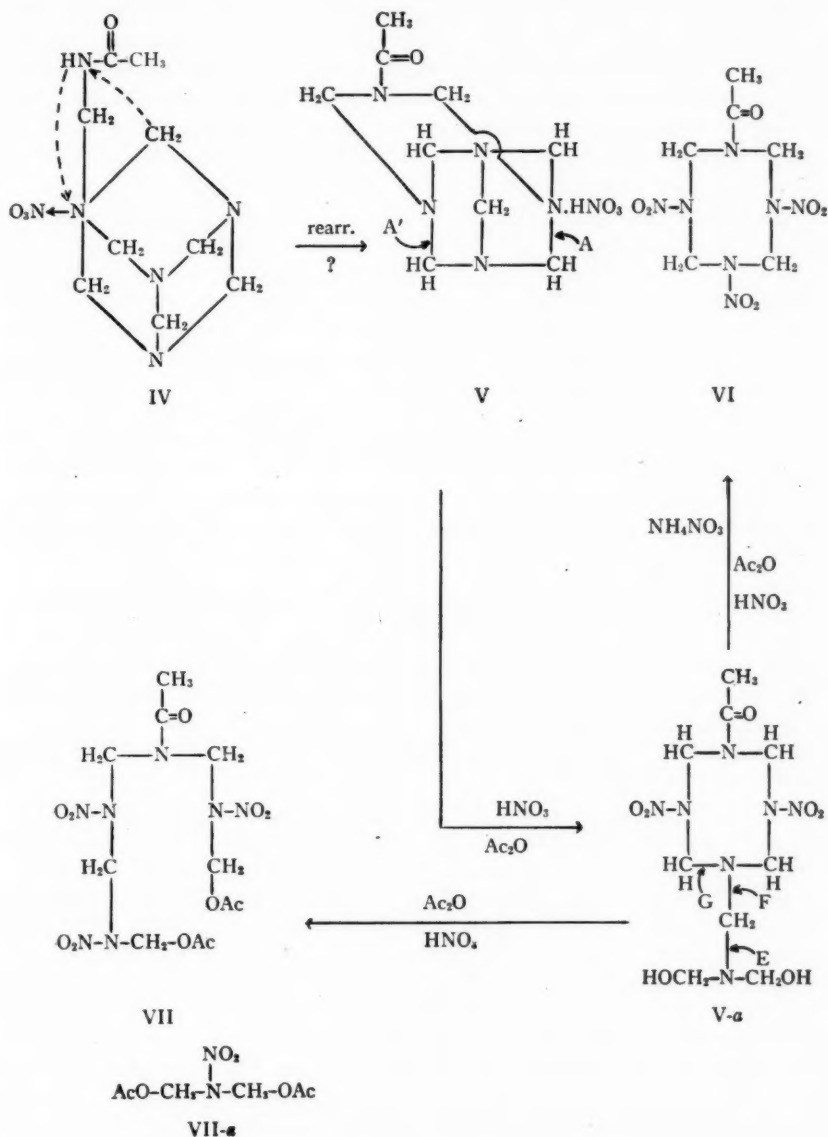
a 17% yield of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, was formed together with a 40% yield of a mixture of Cyclonite and 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane. A rigorous search, however, revealed no isolable amount of the 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X. It would seem then that both of the aceto compounds X and VI were not formed from the same source.

The structure of 1-acetamidomethylhexamine-1 nitrate has been well established (1). We found further confirmation in its inertness toward diazomethane, since hexamine mononitrate was easily converted to hexamine methonitrate by this reagent. Although the evidence for a quaternary salt structure is thus convincing, it is difficult to explain the formation of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, from such a structure. On the other hand, if VI were derived from 1,5-*endomethylene*-3,7-[*endodimethylene*-N-acetamido]-1,3,5,7-tetrazacyclooctane, V, then this latter ternary salt could be considered as a rearrangement product in which a 1,3-shift of methylene was compensated by a 1,3-shift of hydrogen within the quaternary ion, IV. It is interesting to note that the multiple 1,3-shift must occur in this case in the same manner as do all 1,2-rearrangements, i.e., with inversion from tetrahedral apex to base. The rearrangement is illustrated by the dotted arrows in IV.

Under any circumstances V represents a reasonable structure from which VI can be derived by nitrolysis without any concurrent production of acetodinitrotriazacyclohexane, X. Thus by complete analogy with the nitrolysis of hexamine (16) the initial scission can be specified at A,A' in V. If esterification is hindered in V-a (by presence of ammonium nitrate) then demethylation can occur until linkage F is reached, after which nitration will give acetotrinotetrazacyclooctane, VI. If esterification is possible in V-a (absence of ammonium nitrate) then scission with esterification will occur at E and subsequently at G. This would account for the reaction product 1,9-diacetoxy-6-aceto-2,4,8-trinitro-2,4,6,8-tetrazanonane, VII, which was isolated by Carmack and associates when they treated IV (or hexamine) with nitric acid and acetic anhydride (9). We have repeated their preparation to obtain a 51% yield of VII from IV and also a 36% yield of the other fragment, diacetoxydimethylnitramine, VII-a.

The enhancement in yield of IV from hexamine, nitric acid, and acetic anhydride when acetamide is included with these reagents (1) strongly recommends V as the intermediate from which acetotrinotetrazacyclooctane, VI, is formed in the Bachmann reaction, since the yield of VI is likewise increased when acetamide is added to the Bachmann ingredients. Earlier in the present report it has been shown that the effect of this included acylamide was independent of the anhydride. The relationship of this effect to the formation *in situ* of IV was obtained by treating a homologue of IV, propanoylamidomethylhexamine-1 nitrate (1), with acetic anhydride, ammonium nitrate, and nitric acid under Bachmann reaction conditions; then alternatively IV was treated with propionic anhydride, ammonium nitrate, and nitric acid. In

addition to Cyclonite and 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane there were obtained from the two reactions specifically 1-propanoyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, and 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, respectively. Neither product was contaminated with the other.



Although 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X, could not be obtained from the compound that Bachmann and coworkers designated as IV, it was found that a 3 to 5% yield of X could be obtained, in addition to Cyclonite, when 3,7-*endomethylene*-1,5-diaceto-1,3,5,7-tetrazacyclooctane, VIII (10), was nitrolyzed under conditions of the Bachmann reaction. The actual yield was probably higher than the 3 to 5% which was isolated, since contamination with unidentified impurities made the separation difficult. However, this difficulty would not invalidate our assurance that none of the acetotrinitrotetrazacyclooctane, VI, was present in this reaction mixture. None of VI would be expected if VIII has the structure assigned to it. This assigned structure explains, by nitrolysis at G and G', the formation of 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X.

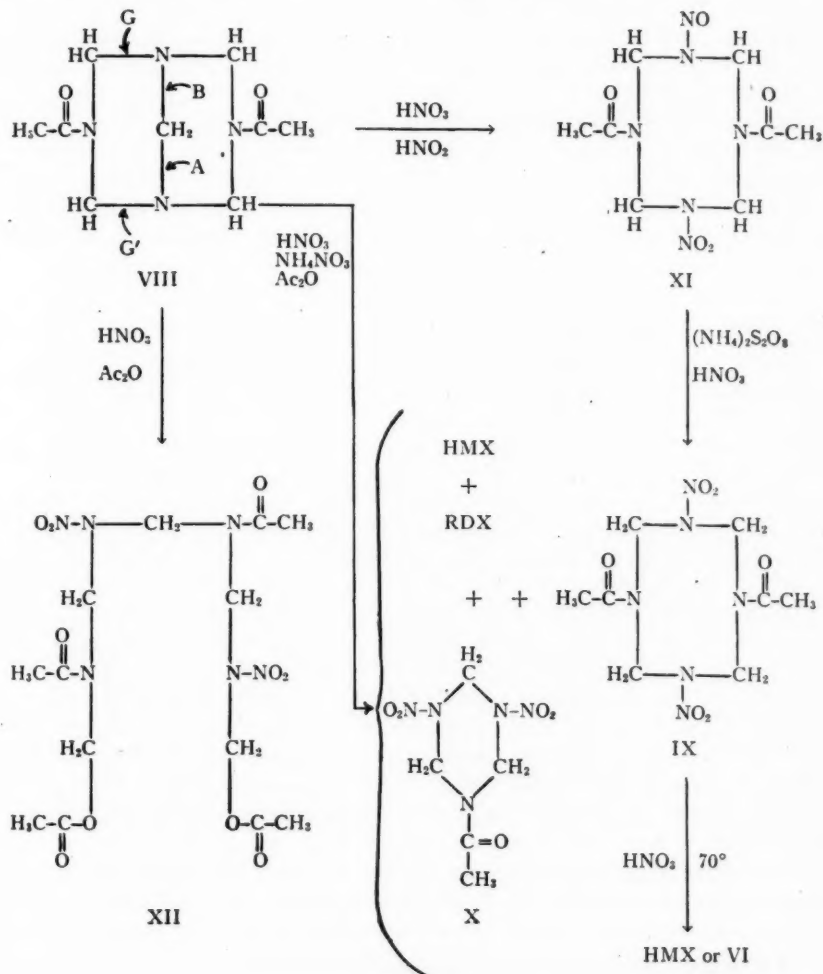
Instead of VI a high melting compound was found in 4 to 7% yield. Its empirical formula was $C_8H_{14}N_6O_6$. Since this compound possessed the same solubility characteristics as 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) it was difficult to free it from this contaminant. The compound was finally obtained in a state of purity by the following alternative method of preparation: the oxidation of 1,5-diaceto-3-nitroso-7-nitro-1,3,5,7-tetrazacyclooctane, XI, by ammonium persulphate (7) in nitric acid yielded the same high melting compound in 77% yield. Since 1,5-diaceto-3-nitroso-7-nitro-1,3,5,7-tetrazacyclooctane, XI, had also been prepared from 3,7-*endomethylene*-1,5-diaceto-1,3,5,7-tetrazacyclooctane (12), VIII, this established the structure of the new compound as 1,5-diaceto-3,7-dinitro-1,3,5,7-tetrazacyclooctane, IX.* Its mode of formation from VIII is evident (by analogy with the formation of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (6)) as scission at A in structure VIII followed by demethylation and nitrolysis at B. Finally IX was characterized by its conversion to 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, or to 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX), depending on the temperature at which the nitration was carried out. Carmack and his coworkers prepared, in small yield from 3,7-*endomethylene* 1,5-dinitro-1,3,5,7-tetrazacyclooctane and acetic anhydride, a compound melting at 257° C. (4). We have purified their compound rigorously and find it to be identical with IX.

This intercorrelation among related structures was established in another way. It has been found (1, 15) that elimination of ammonium nitrate from the set of Bachmann reagents induces alternative scission of the cyclic structures of the hexamine type. Thus 3,7-*endomethylene*-1,5-dinitro-1,3,5,7-tetrazacyclooctane (DPT) reacts with nitric acid and acetic anhydride to give the linear polymethylenenitramine 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (15). When 1,5-diaceto-3,7-*endomethylene*-1,3,5,7-tetrazacyclooctane, VIII, was treated with these reagents a compound was obtained which ought, on the basis of its elemental analysis, to be 1,9-diacetoxy-2,6-diaceto-4,8-dinitro-2,4,6,8-tetrazanonane, XII. This would be the

* It also confirmed, by intercorrelation, the structure for VIII for which the nitrogen analyses were never entirely satisfactory until Kjeldahl rather than Dumas analyses were carried out.

expected compound if nitrolysis and esterification occurred at A in structure VIII, then subsequently at G.

We have thus shown that the aceto compounds VI and X can be prepared under the conditions of the Bachmann reaction from the two progenitors, IV (or V) and VIII, which in turn have, up to the present, only been prepared from hexamine. While one of the two aceto compounds, 1-aceto-3,5-dinitro-1,3,5-triazahexane has been prepared by acetylation of 3,5-dinitro-3,5-diazapiperidinium nitrate (19), no comparable synthesis of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, exists. It is reasonable to assume that both



compounds are formed in the same manner since they always exist together. The preponderance of evidence with respect to these aceto compounds, as well as with the other by-products and main products of the Bachmann and Schiessler-Ross reaction, is in favor of their synthesis by selective nitrolytic and acetolytic degradation of hexamine rather than by stepwise synthesis from its fragments. The Schiessler-Ross reaction may then be considered as the secondary phase of the Bachmann reaction. On this basis the Schiessler-Ross reaction comprises a synthesis of hexamine from formaldehyde and ammonium nitrate together with a nitrolysis of the Hale type by the nitric acid which thus is set free according to Equation II.



In conclusion it should be pointed out that the mechanism of formation of one by-product of hexamine nitrolysis has never been satisfactorily explained. This compound, 3,5-dinitro-3,5-diaza-1-oxacyclohexane (17), has never been synthesized from simpler substances nor produced by degradation of any substance except hexamine. It may be significant that it never is encountered under conditions to which one can refer as those of Bachmann or of Schiessler and Ross but only those of Hale. Until the genesis of this compound is satisfactorily explained, however, one cannot consider the nitrolysis of hexamine as completely elucidated.

Experimental*

Nitrolysis of Hexamine with the Schiessler-Ross Reagents at 25° C.

Finely ground ammonium nitrate, 32 gm. (0.4 mole) and 18 gm. (0.6 mole) of Roessler and Hasslacher paraform were added to 21 cc. (0.37 mole) of acetic acid and 95 cc. (1 mole) of acetic anhydride. This suspension was stirred for 19 hr. at 25° C., then diluted with a solution of 300 cc. water and 10 cc. of 70% nitric acid at 60° C. This was stirred for 15 min. at 35° C., cooled to 0° C. and filtered to remove 4.77 gm. An aliquot of this sticky precipitate was found by hot digestion with 70% nitric acid to contain 32% of its weight as crude Cyclonite, m.p. 189° to 190° C. This represents a yield 5.2% of theoretical on the ammonium nitrate basis. The Cyclonite was separated by hot methanol extraction to leave an insoluble amorphous residue with elemental analysis conforming to $\text{C}_7\text{H}_{15}\text{N}_8\text{O}_{11}$. It was insoluble in alkali, acid, ethanol, nitromethane, acetic acid, benzene, and dioxane but could be separated by boiling acetic anhydride into 30% of material melting at 232° to 233.5° C. (decomp.) with elemental composition conforming with $\text{C}_3\text{H}_6\text{N}_3\text{O}_4$ and 70% which decomposed without melting at 281° to 296° C. The elemental analysis of this latter material conformed with $\text{C}_{11}\text{H}_{24}\text{N}_{15}\text{O}_{16}$. A large amount of formaldehyde was lost during the separation with acetic anhydride.

The acidic aqueous filtrate from which the crude precipitate had been removed was neutralized to pH 6 with 28% ammonia. The sticky solid which precipitated weighed 5.56 gm. It was separated by 25 cc. of warm ethanol

* All melting points have been corrected against reliable standards.

into 3.86 gm. of insoluble material melting at 195° to 196° C. (decomp.). This represents an 18% yield (ammonium nitrate basis) of 1,5-dinitro-3,7-endomethylene-1,3,5,7-tetrazacyclooctane since its mixed melting point with this substance was not lowered. The alcoholic solution was cooled and evaporated to yield 0.77 gm. of crude 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane, II, (R=Ac), or 1.4% of theoretical (ammonium nitrate basis). This was purified to melt at 104° to 105° C. by crystallization from ethanol. The mixed melting point with authentic material was not lowered.

Methylene Diacetate in the Schiessler-Ross Reaction

In order to avoid an induction period in this test reaction, a normal 0.1 molar (18) reaction was carried out. With the temperature still maintained at 69° to 70° C. a solution of 0.1 mole methylene diacetate (n_D^{24} 1.4125), 0.1 mole acetic acid, and 0.26 mole of acetic anhydride was added over a 20 min. period while five 1.60 gm. portions of ammonium nitrate were introduced over the same time. There was no characteristic heat evolution during this addition. Subsequent processing gave Cyclonite in yield of 47% on the basis of the paraform used in the initial step. The methylene diacetate thus does not contribute to Cyclonite formation.

1,3-Dinitro-5,7-dimethyl-1,3,5,7-tetrazacyclooctane, III.

A solution of 1.36 gm. (0.01 mole) of methylenedinitramine (5) in 4.5 cc. (0.06 mole) of 40% formalin was allowed to stand at 25° C. for 10 min. It was then cooled to 0° C. and treated with 2.1 cc. (0.02 mole) of 30% aqueous methylamine. The precipitate, which separated immediately, was filtered after the reaction mixture had aged for 20 min. more at 0° C. This product weighed 1.13 gm. and melted at 91° to 93° C. (decomp.). It was extracted with 8 ml. of absolute ethanol at 25° C. to yield a solution which was evaporated to dryness in an air stream. The residue weighed 0.04 gm. and melted at 108° C. (decomp.). This thermally unstable compound was analyzed without further purification. Its yield was further augmented to about 25% of theoretical by further ethanol and acetone extraction of the residue. Calc. for $C_6H_{14}N_6O_4$: C, 30.7; H, 6.04; N, 35.8%. Found: C, 31.1; H, 6.13; N, 35.3%. The residue from the ethanol extraction was further washed with ethanol and acetone until the melting point could not be raised above 134° to 135° C. The remainder weighed 0.75 gm. The structure of this compound has not been ascertained. Calc. for $C_6H_{14}N_9O_{10}$: C, 19.4; H, 3.77; N, 33.8%. Found: C, 19.4; H, 3.79; N, 34.3%.

Methylenedinitramine with Formaldehyde

Methylenedinitramine, 0.22 gm. (0.0016 mole), was dissolved in 0.24 cc. (0.0032 mole) of 40% formalin at 0° C. and one drop of pyridine was added. A solid settled out over a period of two or three days at 0° C. and after nine days the amorphous material was filtered, ground up with 25 cc. of water, and dried at 50° C. Weight of the product was 0.19 gm.; decomposition range was 219° to 230° C. (brown residue). Yield is 86% by weight on the methylenedinitramine. A portion, 0.16 gm., of this product was suspended in 10 cc.

of acetone at 25° C. and the residue (0.11 gm.) was extracted with 6 cc. of boiling ethanol and two 5 cc. portions of boiling acetone. The residue which remained decomposed to a brown residue over a range of 216° to 228° C. and was found to have the following analysis. Calc. for $C_6H_{12}N_9O_{10}$: C, 16.7; H, 3.36; N, 35.2%. Found: C, 16.4; H, 3.257; N, 34.8%.

This product was completely destroyed in boiling 70% nitric acid, indicating the absence of RDX. It is insoluble in boiling acetone, ethanol, benzene, and nitromethane. It is somewhat soluble on standing in 99% nitric acid at 25° C. and is recovered on dilution with water in yields of 70% to 80%. It is evidently a methylenedinitramine-formaldehyde polymer.

Addition of Methylenedinitramine to the Schiessler-Ross Reagents

A finely ground mixture of 10 gm. of ammonium nitrate (0.125 mole), 3 gm. (0.1 mole) of Roessler and Hasslacher paraform and also 2.72 gm. (0.02 mole) of methylenedinitramine, m.p. 101° C., were added equivalently and proportionately with stirring to a solution of 5.7 cc. (0.1 mole) of acetic acid in 25 cc. (0.26 mole) of acetic anhydride at 70° C. over a period of 14 min. The reaction mixture was stirred 30 min. longer at 70° C. and then cooled to 0° C. and the precipitate filtered and water-washed. Weight of the product was 6.0 gm., m.p. 190° to 196° C. (shrinkage 189° C.). Yield calculated as crude Cyclonite is 81.2% of theory (formaldehyde basis). This crude product was found to contain 92% Cyclonite-HMX by "fume off" with 70% nitric acid, m.p. 196° to 202° C. The filtrate was neutralized to pH 6 with 28% ammonia and no precipitate of DPT was obtained. If the methylenedinitramine had not been added to this otherwise normal Schiessler-Ross reaction mixture, the yield of crude Cyclonite would have been 58%. The following procedure describes the behavior when methylenedinitramine is used and the paraform is omitted.

To a solution of 2.9 cc. (0.05 mole) of acetic acid in 12.5 cc. (0.12 mole) of acetic anhydride which was warmed to 70° C. was added with stirring a mixture of 5.0 gm. (0.063 mole) of ammonium nitrate and 2.72 gm. (0.02 mole) of methylenedinitramine over a period of 14 min. at $70 \pm 1^\circ$ C. The reaction mixture was stirred 90 min. longer at 70° C. and then diluted with 50 cc. of water, cooled to 20° C., and the precipitate filtered. Weight was 80 mgm., m.p. 200° to 202° C. The filtrate was neutralized to pH 6 with 28% ammonia and allowed to stand at 0° C. for two hours. The precipitate which settled out was filtered, water-washed, and dried at 50° C. Weight was 0.11 gm., m.p. 161° to 182° C. This was separated by crystallizations from ethanol into 65 mgm. of Cyclonite, m.p. 194° to 197° C. and 12 mgm. of crude 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane, m.p. 95° to 97° C. The total yield of Cyclonite is then 0.145 gm. (9.7% of theoretic, methylene basis). The yield of crude 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane is 0.65% of theory (methylene basis).

Preparation of 1,5-Diacetoxy-2,4-dinitro-2,4-diazapentane

To a solution of 2.72 gm. (0.02 mole) of methylenedinitramine in 3 cc. (0.04 mole) of 40% formalin at 25° C. was added 3.28 gm. (0.04 mole) of anhydrous sodium acetate and 20 cc. (0.2 mole) of acetic anhydride. The resulting mixture was warmed to 95° C. for one hour, drowned in 85 cc. of ice-water mixture and neutralized to pH 6 with 28% ammonia. The flocculent precipitate was filtered after standing overnight at 0° C., water-washed, and dried at 50° C. Weight of product was 2.15 gm. The material did not seem to melt or decompose below 275° C. This product was separated by crystallizations from acetone and ethanol into a 9% yield of 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane, m.p. 90° to 92° C., (1 : 1 molar basis) and 1.15 gm. of acetone insoluble compound which decomposed to a brown solid residue over a range of 280° to 315° C. It burst into flame on being heated on a hot spatula and burned like cordite. It could not be detonated by striking on the anvil with a hammer. The material was insoluble in 5 *N* nitric acid and gave a negative test for sodium. It was purified by extraction with boiling acetic anhydride and analyzed. Calc. for $C_{11}H_{24}N_{16}O_{16}$: C, 21.3; H, 3.86; N, 33.7%. Found: C, 21.2; H, 3.84; N, 33.4%.

Attempted Synthesis of 3,5-Dinitro-3,5-diaza-1-oxacyclohexane (17)

A solution of 0.68 gm. (0.005 mole) of methylenedinitramine in 0.9 cc. (0.012 mole) of 40% formalin was added rapidly to 22.4 cc. (0.5 mole) of 95% nitric acid which had been cooled to 0° C. The solution was allowed to stand in an ice-bath for 40 min. and then drowned in 40 cc. of ice-water mixture. The precipitate which settled out was washed acid-free with water and dried over phosphorus pentoxide *in vacuo*. Weight was 0.31 gm., m.p. 112° to 115° C. (decomp.). Yield calculated as 1,5-dinitroxy-2,4-dinitro-2,4-diazapentane is 22% of theory (methylenedinitramine basis). This material was identified as 1,5-dinitroxy-2,4-dinitro-2,4-diazapentane by mixed fusion with an authentic sample and also by its conversion to the dimethoxy derivative on treatment with boiling methanol. The drowned acid filtrate from this reaction was neutralized to pH 6.5 with 28% ammonia and then extracted with chloroform. The chloroform extracts were found to contain no 3,5-dinitro-3,5-diaza-1-oxacyclohexane.

Other attempts to prepare this compound by treating both 1,5-dinitroxy-2,4-dinitro-2,4-diazapentane and 3,5-dinitro-3,5-diazapiperidinium nitrate with 92% and 95% nitric acid failed to give the desired product. We were likewise not able to dehydrate a solution of 1 mole of methylenedinitramine in 2 moles of 40% formalin to 3,5-dinitro-3,5-diaza-1-oxacyclohexane by vacuum evaporation at 60° to 100° C. over a four hour period.

1-Aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI

A solution 33.6 gm. (0.24 mole) of hexamine in 160 cc. (2.8 moles) of acetic acid was added simultaneously, equivalently, and continuously with a solution of 38.4 gm. (0.48 mole) of ammonium nitrate in 46.5 cc. (1.1 moles) of 99% nitric acid into 640 cc. (6.18 moles) of well stirred acetic

anhydride at 65° C. The temperature during the 20 min. addition period was held at 69° ± 2° C. The solution was aged 20 min. longer at 65° ± 2° C. and then diluted slowly with 1200 cc. of water, cooled to 20° C., and was filtered. The yield of crude Cyclonite was 52.8 gm., m.p. 192° to 198° C. (soft 189° C.) or 50% on the formaldehyde basis.

The filtrate was neutralized to pH 5.6 with 28% ammonia. After five days at 2° C., 9.1 gm. of solid, m.p. 181° to 194° C. (soft 175° C.), settled out. This crude VI was suspended in 30 cc. of acetone and boiled for a few minutes. The insoluble residue melted at 213° to 214° C. (wt. 2.31 gm.) while the solution on cooling yielded 3.0 gm., m.p. 215° to 217° C. The total crude yield of 5.3 gm. was 7.5% on the hexamine basis.

The crude compound was crystallized several times from acetone and nitromethane to melt at 224.2° to 224.7° C. with frothing. The compound is slightly soluble in pyridine, acetone, and nitromethane, but almost insoluble in ethanol, benzene, acetic acid, and ether. It is destroyed readily by hot 70% nitric acid and warm 10% aqueous sodium hydroxide. It decomposes slowly in 28% ammonia. It can be detonated by a hammer blow on the anvil. Calc. for $C_6H_{11}N_7O_7$: C, 24.6; H, 3.76; N, 33.4%. Found: C, 24.9; H, 3.75; N, 33.6%.

A positive test for acetate could be obtained by decomposing 1 gm. of VI in 10 cc. of 96% sulphuric acid at 20° C. After frothing had ceased, the solution was cooled, diluted with 6 cc. of water, refluxed 15 min. and then distilled. The distillate, which gave a positive lanthanum nitrate test for acetic acid (11), was titrated with 0.1 *N* aqueous sodium hydroxide using phenolphthalein to indicate 92% of the acetyl expected if VI contains one acetyl group. The neutralized solution was evaporated and treated with *p*-bromophenacyl bromide to yield the identifying acetate.

The acetic acid was identified also through the reaction of VI with 98% nitric acid. A 25% yield of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane could be isolated (m.p. 278° C.) by treatment at 5° C. (subsequently at 55° C.) with 33 equivalents of 98% nitric acid. After this compound was filtered from the alkali-neutralized liquor, the filtrate was boiled under reflux with 276 gm. of ferrous sulphate and an excess of sulphuric acid until the brown fume ceased to be evolved. The acetic acid was finally distilled off in quantity and identity as outlined above.

1-Aceto-3,5-dinitro-1,3,5-triazacyclohexane, X

When the neutralized filtrate from which VI is filtered was allowed to stand for 19 days, a further 2.45 gm. of material was precipitated. When this was combined with the evaporated mother liquors from which VI was crystallized, then ground and centrifuged in an ethylene dibromide - petroleum ether mixture of density 1.71, a layer less dense than this medium could be separated from the top. The 1.8 gm. (m.p. 136° to 138° C.) so obtained was repeatedly crystallized from ethanol and 1:1 ethanol:acetone to melt at 158° C.

Calc. for $C_5H_9N_5O_5$: C, 27.4; H, 4.14; N, 31.9; CH_3COO , 19.6%. Found: C, 27.4; H, 4.14; N, 31.9; CH_3COO , 19.1%.

The molecular weight was first determined reproducibly by the micro-Rast method in camphor as 262, but later it was found that if the camphor solution of X were heated for 10 to 15 min., another reproducible value of 220 (calculated for $C_5H_9N_5O_5$, 219) was obtained. This behavior is undoubtedly owing to incompleteness of apparent solution and seems to be characteristic of many cyclic nitramines.

When 1 gm. of X was boiled 17 hr. with 50 cc. of *N*/2 sulphuric acid (solution after 15 min.), analysis for formaldehyde by the dimedone method and for ammonia by the Kjeldahl method gave values of 39.3% CH_2O and 8.9% NH_3 (calc. for $C_5H_9N_5O_5$: CH_2O , 41.1; NH_3 , 7.8%). Decomposition of X in 96% sulphuric acid with subsequent dilution and distillation gave Duclaux numbers characteristic for acetic acid. Identification was also effected by the *p*-bromophenacyl ester.

When 0.5 gm. of X was added to 5.9 cc. of 99% nitric acid at 65°C. and digested at this temperature over a 30 min. period, dilution gave 0.25 gm. of a crude product, m.p. 178° to 194° C., from which a 38% yield of Cyclonite m.p. 201° to 204° C. was obtained after digestion with hot 70% nitric acid.

Compound X could also be prepared from 3,5-dinitro-3,5-diazapiperidinium nitrate (19). Cyclonite (19) is the main product when the amine nitrate is heated in acetic anhydride alone. The addition of 0.41 gm. (0.005 mole) of sodium acetate to 3 cc. (0.053 mole) of acetic acid and 6.0 cc. (0.06 mole) of acetic anhydride, on the other hand, gave a solution which was stirred at 25° C. for nine hours with 1.2 gm. (0.005 mole) of the dinitrodiazapiperidinium nitrate. This reaction mixture, when diluted into 50 cc. of ice and water and neutralized with 28% ammonia to pH 5.6, gave 0.51 gm. of precipitate after four hours at 2° C. This melted at 151° to 153° C. when water-washed and dried at 95° C. Purification of this 46% yield in boiling ethanol raised the melting point to 156° C. (if the amine nitrate, m.p. 99° to 100° C. was free from Cyclonite), and it could thus be identified by mixed melting point.

A third method of preparation of X has been described previously (8) from methylene-bis-1-[3,5-dinitro-1,3,5-triazacyclohexane].

Addition of Acetamide to Bachmann Reagents

A solution of 2.52 moles of ammonium nitrate in 4.06 moles of 99% nitric acid and a solution of 1 mole of hexamine and 1 mole of acetamide in 11.65 moles of acetic acid was added proportionately over 45 min. from two burettes to 9.3 moles of stirred acetic anhydride at 65° C. The yield of crude Cyclonite, m.p. 178° to 180° C. (which separated after the mixture was heated 10 additional minutes, then diluted fivefold with water and let stand at 0° C. overnight was 58.3% of theoretical.

A suspension of 20 gm. of this product in 20 cc. of acetone was filtered and washed slowly with five 10 cc. portions of the same solvent. There remained 14.1 gm. of Cyclonite, m.p. 197° to 198° C. (soft at 188° C.). The filtrate was

evaporated to yield 0.62 gm. of material, m.p. 221° C. After crystallization from nitromethane it melted at 223° C. and did not depress the melting point of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacycloöctane, VI.

Further concentration of the acetone solution yielded 1.80 gm. which on crystallization from nitromethane turned out to be 30% of VI and 70% of Cyclonite plus 1,3,5,7-tetranitro-1,3,5,7-tetrazacycloöctane, HMX. The remaining mother liquors were evaporated and the residue fractionally crystallized from 1 : 1 ethanol-acetone to yield 0.25 gm. of impure VI, m.p. 214° to 215° C. and 1.78 gm. having approximately the composition of the original mixture. The remainder of the mother liquor yielded 0.69 gm. of impure 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X, melting at 140° to 160° C. from which the pure compound, m.p. 158° C., was isolated by ethanol crystallization and identified by mixed melting point.

Since 1.78 gm. of the fractionally crystallized material can be considered as not separated, the distribution of the remaining 18.22 gm. may be estimated as follows:

Cyclonite plus tetranitrotetrazacycloöctane	15.70
1-Aceto-3,5,7-trinitro-1,3,5,7-tetrazacycloöctane, VI	1.47
1-Aceto-3,5-dinitro-1,3,5-triazacyclohexane, X	0.69
Unaccounted	0.36

These quantities represent 8.5% and 3.5% yields (1 : 1 basis) of VI and X respectively.

Effect of Ammonium Nitrate-Nitric Acid Ratio on Yield of VI

In a typical preparation of Cyclonite by the Bachmann procedure, 160 cc. (1.70 moles) of acetic anhydride was charged into the stirred reaction flask and the temperature raised to 68° C. Thereupon, 48.5 gm. (0.606 mole) ammonium nitrate previously dissolved in 41 cc. (0.975 mole) of 98% HNO₃ and 33.6 gm. (0.24 mole) of hexamine dissolved in 160 cc. (2.8 moles) of acetic acid were measured proportionately from the burettes with the nitric acid solution leading by 5% (vol.). When the water bath was lowered approximately to 45° C., the temperature of the reaction could be regulated conveniently between 65° and 70° C. by controlling the rate of addition. Under these circumstances, between 15 and 20 min. was usually required to complete the addition. The reaction mixture was then heated to 90° C. with stirring before dilution with 400 cc. of hot water. The first 15 cc. of water was added slowly to determine whether any free anhydride remained. The diluted solution was then simmered at 90° C. for at least one-half hour; during this period considerable gassing could be observed if the stirring were stopped. After pouring in an additional 250 cc. water, the mixture was cooled to 0° C. usually overnight. After suction filtration, the product was washed neutral to bromocresol green with about one liter of water and dried by air draft.

The 1,3,5,7-tetranitro-1,3,5,7-tetrazacycloöctane, HMX, in this crude Cyclonite was determined on a sample obtained by evaporation of an acetone solution followed by centrifugation of the ground residue in iodobenzene.

The tetranitro compound was more dense than 1.83, and therefore settled to the bottom of the tube.

The relative yield of VI was obtained by filtration of the diluted reaction filtrate aliquots after 30 days.

The variations in ammonium nitrate-nitric acid ratio are shown in Table II.

TABLE II

Moles HNO ₃	Moles NH ₄ NO ₃	Mole ratio HNO ₃ /NH ₄ NO ₃	Yield crude Cyclonite	% HMX in crude Cyclonite	Wt. yield of VI, mgm.
4.63	2.0	2.31	77	5	20
4.30	2.0	2.15	73	9	0
4.06	2.0	2.03	69	13	310
4.06	2.04	1.98	69	13	505
4.06	2.08	1.96	75	10	560
4.06	2.08	1.96	70	12	470
4.06	2.20	1.85	74	11	460
4.06	2.52	1.61	80	6	285
4.06	2.79	1.46	70	7	70

1-Propanoyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane

The preparation involving added acid amide (outlined above) was repeated with the exception that propionamide was used instead of acetamide. After removal of a crude Cyclonite yield (m.p. 198° to 201° C.) of 39% the filtrate was neutralized to pH 5.6 with ammonia and evaporated under 11 mm. almost to dryness. The crystal residue was stirred with 500 cc. water and then filtered to remove material melting at 161° to 165° C. which contained 32% of Cyclonite according to the weight of residue obtained after oxidation with hot 70% nitric acid. The crude was crystallized from acetone and nitromethane to melt at 199° to 200° C. This new compound was produced in 8.5% yield on the basis that it was the only product except Cyclonite which was present in the crude material obtained by neutralization of the reaction liquor. Calc. for C₇H₁₃N₇O₇: C, 27.4; H, 4.24; N, 31.8; CH₂O, 39.1; NH₃, 5.54%. Found: C, 27.6; H, 4.24; N, 31.8; CH₂O, 36.3; NH₃, 5.82%. The compound, after decomposition with 96% sulphuric acid, gave Duclaux numbers expected for propionic acid, and *p*-bromophenacyl propionate was prepared from the neutralized Duclaux distillate. The compound could be converted in 26% yield to tetranitrotetrazacyclooctane (HMX) by treatment of 0.48 gm. (0.0016 mole) in 5.5 cc. (0.13 mole) of 98% nitric acid at 40° C. for 20 min., followed by dilution with water.

Addition of Benzamide to Bachmann Reagents

When one equivalent of benzamide was added in acetic acid solution proportionately to the other reactants in the Bachmann reaction a 40% crude yield of Cyclonite was obtained on cooling to 20° C. after dilution. A second crop of material was obtained by chilling the filtrate to 0° C. This was found

chiefly to be methylene-bis-benzamide (20 gm. from 33 gm. of hexamine) contaminated with a yellow gum from which it was separated by elution with 2-nitropropane. The purified product melted at 223° to 224° C.

Preparation of Acetamide

A. An 83% yield of acetamide, m.p. 81° to 82° C., could be obtained by stirring 1 equivalent of dry ammonium acetate into 3.5 equivalents of acetic anhydride at 57° C. The temperature of the mixture rose to 71° C. during solution of the salt, and then cooled rapidly. The clear cold solution was evaporated at 25° C. under 760 mm. (atmospheric) to yield pure acetamide.

B. A total of 0.312 mole of ammonium nitrate was heated for 10 hr. with a stirred mixture of 1.7 moles of acetic anhydride and 1.75 moles of acetic acid. This total was added in portions of 0.15 mole at zero time, 0.08 mole after two hours and 0.08 mole after the next hour. The nitrate had all dissolved after four hours. No precipitate appeared after the solution was finally cooled. Distillation at 70° C. under 15 mm. yielded 10 to 15 cc. of yellowish liquid; subsequent distillation at 120° C. yielded 1.35 gm. of acetamide, m.p. 81° to 82° C. (m.m.p.). This yield of 7% may be low because of losses in transfer but could not have exceeded 15%. A small amount of dark brown residue remained in the flask.

When this procedure was varied by concomitant addition of 0.815 mole of 98% nitric acid with the other reagents, no acetamide was obtained; upon cooling, a large part of the ammonium nitrate precipitated. By air evaporation 84.5% was recovered, m.p. 167° to 169° C.

1,5-Diaceto-3,7-endomethylene-1,3,5,7-tetrazacyclooctane, VIII

To 300 gm. (3 moles) of stirred acetic anhydride was added 140 gm. (1 mole) of hexamine. An ice-bath was applied immediately to prevent temperature rise above 56° C. After two hours the reaction mixture had cooled to 25° C. and 100 cc. of ethyl ether was then added. The filtered precipitate, washed with absolute ethanol, weighed 13.7 gm. and melted at 180° C. Crystallization from absolute ethanol gave 9.07 gm. melting at 193.8° to 194° C. The crude yield was 6.5% of theoretical. When addition of hexamine was gradual so that the reaction temperature did not rise above 40° C. the yield was 5.2%. When cooling was not applied and the temperature rose to 95° C., no product at all was obtained. Likewise none of the compound was formed when the gradual addition was carried out while 89 gm. (1 mole) of methylolacetamide was added equivalently (temp. 40° C.).

Repeated purification by solution in chloroform (4 cc. per gm.) and crystallization following addition of 1 volume of ether failed to raise the melting point. After solution in nitromethane (3.5 cc. per gm.) followed by dilution with ether (5.8 cc. per gm.) it melted at 194.0° to 194.2° C. The compound was recovered unchanged after treatment of its chloroform solution with an excess of diazomethane in ether. It was also recovered unchanged by chloroform extraction of its aqueous solution to which one equivalent of alkali had

been added. Calc. for $C_9H_{16}N_4O_2$: C, 50.9; H, 7.60; N, 26.4%. Found: C, 51.1; H, 7.50; N, 25.4%.

A large number of attempts to prepare VIII by interaction of 5 moles of formaldehyde (as paraform, trioxane, or the monomeric gas) with 2 moles of ammonium acetate and 2 moles of acetamide in acetic acid and/or 5 moles of acetic anhydride at temperatures from 25° C. to 70° C. failed to give a trace of the desired product. The result was the same when acetic acid was omitted and also when methylolacetamide was used instead of acetamide.

1,9-Diacetoxy-2,6-diaceto-4,8-dinitro-2,4,6,8-tetrazanonane

To a suspension of 2 gm. (0.0094 mole) of 1,5-diaceto-3,7-*endomethylene*-1,3,5,7-tetrazacyclooctane in 10 cc. (0.1 mole) of acetic anhydride at 25° C. was added 1.0 cc. (0.024 mole) of 98% nitric acid. After 10 min. at room temperature, the reaction mixture was warmed five minutes on the steam bath and then drowned in 100 cc. of ice and water. It was then neutralized to pH 4 with ammonia. The precipitated oil was converted to a gummy solid which was dissolved in acetone. Dilution with petroleum ether precipitated 1.83 gm., melting 121.5° to 123° C., or 46% of theoretical on the 1 : 1 mole basis. The material melted at 124° to 124.5° C. after three crystallizations from acetone-methanol (55° to 20° C.). Calc. for $C_{13}H_{22}N_6O_{10}$: C, 37.0; H, 5.27; N, 19.9%. Found: C, 37.0; H, 5.42; N, 19.9%. When only half as much nitric acid was used in this preparation there was no water insoluble product. Dilution of the reaction mixture into ether gave an unstable precipitate which dissolved in boiling methanol. After two minutes, this solution also gave no water-insoluble material.

When diacetoxydiacetodinitrotetrazanonane was dissolved at 0° C. in 30 equivalents of 98% nitric acid and the solution (finally at 10° C.) was drowned in water, no insoluble precipitate appeared.

1,5-Diaceto-3-nitroso-7-nitro-1,3,5,7-tetrazacyclooctane, XI

A solution of 11.5 ml. (0.184 mole) of nitrogen tetroxide in 15.5 ml. (0.373 mole) of 98% nitric acid was maintained at 0° C. while 2.41 gm. (0.012 mole) of 1,5-diaceto-3,7-*endomethylene*-1,3,5,7-tetrazacyclooctane, VIII, was added over seven minutes. There was no appreciable heat evolution. After five minutes more at 0° C. the whole was poured into 400 gm. of ice. No precipitate appeared at once in the clear blue aqueous solution, but after 12 hours 2.46 gm. of product was filtered off. This 75% yield of XI melted at 225.2° to 227.2° C. The compound was photosensitive and turned blue on exposure to diffuse light.

1,5-Diaceto-3,7-dinitro-1,3,5,7-tetrazacyclooctane, IX

A solution of 1.0 gm. (0.0037 mole) of the nitroso compound XI in 7.2 ml. (0.16 mole) of 98% nitric acid was prepared cautiously at 2° to 3° C. It was stirred at this temperature while 2.63 gm. (0.012 mole) of ammonium persulphate was added over five minutes. After 15 min. more at this temperature, it was warmed to 20° C., allowed to stand one hour, and then

poured into ice. After 30 min., a precipitate began to appear; this was filtered off after 75 min. It weighed 0.89 gm. or 83% of the theoretical yield. It melted at 262° to 263° C. and was crystallized three times from boiling nitromethane (60 cc. per gm.) to melt at 265.5° to 266° C. This melting point at 2° per minute temperature rise could be raised or lowered by change in rate. Calc. for $C_8H_{14}N_6O_6$: C, 33.1; H, 4.86; N, 28.9%. Found: C, 33.2; H, 4.92; N, 28.7%.

The procedure of Carmack and coworkers (4) was repeated and the product crystallized repeatedly from boiling acetone, m.p. 261° C. A mixed melting point with IX was not lowered.

This compound was converted in 25% yield to 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) by overnight treatment of 0.26 gm. with 4 cc. of 99% nitric acid. The solution was warmed to 70° C. for five minutes and then poured into ice. The crude product (m.p. 258° C.) was purified by crystallization from 70% nitric acid to melt at 275° to 276° C. A mixed melting point with an authentic sample was not lowered.

When this procedure was varied by use of 95% nitric acid and a final warming to 70° C. with immediate dilution into ice, the product melted at 214° C. and weighed 0.06 gm. This was proved to be a 23% yield of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane by mixed melting point determination.

Bachmann Nitrolysis of Diacetoendomethylenetetrazacyclooctane, VIII

To a stirred suspension of 1.76 gm. (0.022 mole) of ammonium nitrate in 5.67 cc. (0.06 mole) of acetic anhydride at 65° to 70° C. were added equivalently 1.25 ml. (0.03 mole) of 98% nitric acid and a solution of 2.12 gm. (0.01 mole) of VIII in 5 cc. of acetic acid over 50 min. After a subsequent 10 min. period 0.54 cc. (0.03 mole) of water was added.

After three hours, the suspension was diluted with 15 cc. water and filtered to remove 0.63 gm. melting at 175° to 190° C., density greater than 1.71. This was crystallized from nitromethane to yield 0.35 gm. of Cyclonite, m.p. 195° to 196° C., mixed melting point not lowered.

The aqueous filtrate was neutralized with 50% aqueous potassium hydroxide to pH 9. Filtration yielded 0.44 gm., m.p. 155° to 210° C. Centrifugation showed that its density was less than 1.71. This was dissolved in 20 to 25 cc. hot nitromethane. On cooling, 0.12 gm. of material, m.p. 261° to 262° C. (soft 253° C.), crystallized out. An additional 0.03 gm. was obtained by concentration of the mother liquors to 2 cc. The total yield was crystallized from hot nitromethane and then from acetic acid (140 cc. per gm.) to melt at 263° to 264° C. A mixed melting point with the compound prepared from XI was not lowered.

The remaining 2 cc. of nitromethane solution, from which was isolated the compound described above, was evaporated in vacuum to dryness. The residue weighed 0.11 gm. and melted at 139° to 149° C. Half of this was heated with 0.5 cc. of 70% nitric acid to yield 18 mgm. of impure Cyclonite,

m.p. 185° to 194° C. The other half was suspended in petroleum ether (b.p. 90° to 100° C.) - ethylene dibromide mixture and centrifuged to give a top layer (0.05 gm.) melting at 141° to 144° C. This was repeatedly crystallized wastefully from nitromethane-ether to give 0.01 gm. melting at 154° C. A mixed melting point with 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X, was not lowered. Yield on the basis of the nitric acid decomposition was estimated as 3% of theoretical. The heavier part of the centrifugate proved by mixed melting point to be Cyclonite.

The ratio of reagents was varied in two additional experiments. The results of all three are recorded in Table III, where all percentage yields are on the 1 : 1 molar basis.

TABLE III
YIELD FROM BACHMANN NITROLYSIS OF 1 MOLE OF VIII

Moles HNO ₃	Moles NH ₄ NO ₃	Moles Ac ₂ O	% RDX	% X	% IX
3	2.2	6	17	3	5.2
3.5	2.2	5.3	14	0.8	14
4	2.2	6	25	5	7

Bachmann Nitrolysis of 1-Acetamidomethylhexamine-1 nitrate, IV

A. With Acetic Anhydride

To a stirred solution of 56.6 cc. (0.6 mole) of acetic anhydride and 50 cc. of acetic acid was added over 45 min. 27.4 gm. (0.1 mole) of IV, while a solution of 17.6 gm. (0.22 mole) of ammonium nitrate in 13.25 cc. (0.32 mole) of 99% nitric acid was added proportionately with respect to the solid. The liquid feed was, however, started ahead of the solid feed so that a 2% lead of the former was maintained over the latter.

The solid dissolved in the reaction mixture until addition was about half complete. After that it only partially dissolved; much foaming accompanied the addition of the last third of the solid. After 15 min. subsequent stirring at the reaction temperature (65° to 68° C.) the mixture was cooled, treated with 40 cc. of water, and then evaporated to dryness under 12 mm. pressure. The residue was covered with 40 cc. of water and neutralized to pH 6.4 with 28% aqueous ammonia. The gummy precipitate solidified completely after 12 hr. stirring, during which colorless gas was evolved. The filtered precipitate was ground, dried, and centrifuged in a medium of density 1.70 (ethylene dibromide - petroleum ether) to yield 9 gm. of impure Cyclonite-tetranitrotetrazacyclooctane (HMX) mixture (m.p. 169° C.) which was heavier than the medium. When an aliquot of this was heated with 70% nitric acid, cooled, and diluted, it yielded the equivalent of 8.6 gm. of uncontaminated RDX-HMX, m.p. 193° C. The centrifugate also contained a layer which was lighter than the medium. It weighed 8.75 gm. (m.p. ca. 110° C.). Both crops were fractionally crystallized from acetic acid, from

nitromethane-acetone and from acetone-ether to yield (in addition to the Cyclonite-HMX) 5.5 gm. of impure 1-aceto-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane, VI, m.p. 210° to 211° C. This was 90% pure (according to the destruction of VI in hot 70% nitric acid) if it contained only Cyclonite and HMX as impurities. This impure material was recentrifuged in the suspension medium of density 1.70 and then was recrystallized from hot nitromethane-acetone (32 cc. and 20 cc. per gm.) to weigh 4.3 gm. and melt at 225.2° C. A mixed melting point with pure VI was not lowered. The yields based on nitric acid fume-off are therefore about 40% of the theoretical (1 : 1 molar basis) as Cyclonite-HMX and 17% as acetotrinitrotetraazacyclooctane, VI.

The evaporated mother liquors from which these substances were isolated were carefully examined by repeated fractional crystallization from ethanol and nitromethane-ether. While there were undoubtedly low-melting compounds present, our experience with the crystallization of 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane persuades us that it was not present.

B. With Propionic Anhydride

When the foregoing procedure was repeated, using propionic rather than acetic anhydride, a fraction melting at 211° to 215° C. was obtained which would represent 5% of the theoretical yield of 1-aceto-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane if it had been pure. According to its decomposition in hot 70% nitric acid it contained about 30% of an RDX-HMX component, m.p. 211° to 218° C. A mixed melting point of the 5% yield with authentic acetotrinitrotetraazacyclooctane was not lowered, whereas a comparable melting point with the propionyl analogue was lowered 15° C. A thorough search of all fractions of the product failed to reveal the presence of 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane.

Nitrolysis of 1-Acetamidomethylhexamine-1 nitrate with Nitric Acid and Acetic Anhydride

To a cold solution of 39.3 cc. (0.39 mole) of acetic anhydride in 20 cc. of glacial acetic acid was added with stirring 13.6 cc. (0.314 mole) of 97% nitric acid. This solution was maintained with stirring at 25° ± 4° C. with a cold water bath while 21.5 gm. (0.0786 mole) of IV, m.p. 174° to 175.5° C. was added over 10 min. The whole was stirred an additional two hours at room temperature and then diluted with 75 cc. of water. This solution was neutralized with 12 gm. (0.3 mole) of sodium hydroxide. The aqueous phase was decanted from the gum which thus was precipitated. The gum was digested a few minutes at 40° C. with 75 cc. ethanol, cooled to 15° C., and the solid filtered and dried. It weighed 23 gm., m.p. 113° to 120° C. (decomp.). Yield as this crude VII is 69% of theoretical (1 : 1 basis). The ethanolic filtrate was combined with the aqueous mother liquor.

The crude VII was dissolved in 125 cc. of warm acetone and precipitated with 125 cc. of warm ethanol to give 17 gm. (51% yield), m.p. 144° to 146° C.

(decomp.). Further crystallizations from acetone raised the melting point to 152–153° C. (decomp.). It was identified by mixed melting point (9).

The combined aqueous ethanol liquors were diluted to 600 cc. with water, and extracted with 175 cc. of ether and then with 300 cc. of petroleum ether (b.p. 60° to 90° C.) benzene (1 : 1). The extracts were combined, washed with two 150 cc. portions of water and then with aqueous sodium carbonate and finally dried over anhydrous sodium sulphate. Distillation of the dried extract at 4.5 mm. gave 5.8 gm. of liquid, b.p. 129° to 136° C. (chiefly at 134° C.). The yield calculated as crude diacetoxydimethylnitramine, VII-a (b.p. 152° C. (10 mm.) when pure) is 36% of theoretical on the 1 : 1 molar basis. This material was identified by conversion (6) to dinitroxydimethylnitramine, m.p. 46° to 49° C., in 35% yield.

Reactions Relating to Structure of 1-Acetamidomethylhexamine-1 nitrate, IV.

The salt, IV, was prepared by adding a solution of 140 gm. (1 mole) of hexamine in 200 cc. of acetic acid over 30 min. to a stirred solution of 98 cc. (1 mole) of acetic anhydride and 63 gm. (1 mole) of 97% nitric acid, previously prepared at 0° to 10° C. and maintained below 35° C. After five hours at 25° C., 100 cc. of ethyl ether was added. The gummy precipitate which formed over 12 hr. was dissolved in 270 cc. of water, and 900 cc. of 95% ethanol was added. Filtration at 10° C. after three hours yielded 86 gm. melting at 172.3° to 172.8° C. or 31% of the theoretical.

When 0.27 gm. (0.001 mole) of this compound was dissolved in 36 cc. (0.001 mole) of saturated aqueous styphnic acid solution an immediate precipitate amounting to 0.32 gm. of hexamine styphnate appeared. This 83% yield melted at 194° C. and was identified by mixed melting point.

When 0.05 mole of the salt IV was dissolved in 30 cc. of water at 0° C. it required only 0.0375 mole of alkali before a pH of 10.5 was reached. The odor of formaldehyde was apparent. The solution was evaporated to dryness under 12 mm. pressure and the residue eluted with 50 cc. of hot chloroform. Evaporation of this solvent yielded 6.38 gm. of impure hexamine. The basicity of the amine could therefore not be determined, since it was not stable, but a *M*/10 aqueous solution free from carbon dioxide, was tested against a glass electrode to show a pH of 6.99.

When a solution of 0.004 mole of IV in 9 cc. water and 10 cc. of ethanol at 0° C. was treated with 0.0045 mole of diazomethane in ether, the solution became colorless in 90 sec. but 75% of pure IV could be recovered from the gummy product. None could be recovered from the colorless solution after 0.02 mole of diazomethane was added to a similar water-ethanol solution of IV over 22 min.

By contrast a solution of 0.004 mole of hexamine mononitrate in 9 cc. water and 10 cc. of ethanol reacted instantly with 0.0045 mole of ethereal diazomethane. When the solution medium was altered to 3 cc. water and 13 cc. of ethanol, evaporation of the solution after diazomethane treatment left a

residue from which 36% of the theoretical yield of hexamine methonitrate could be obtained by crystallization from ethanol.

Bachmann Nitrolysis of 1-Propionamidomethylhexamine-1 nitrate

The Bachmann nitrolysis was effected with 0.44 mole acetic anhydride in 34 cc. acetic acid, 0.15 mole ammonium nitrate in 0.22 mole 99% nitric acid and 0.068 mole of 1-propionamidomethyl-hexamine-1-nitrate (1), m.p. 177° to 178° C. The crude product (14.4 gm., m.p. 162° to 172° C.) was found to contain 60% of the theoretical yield of RDX-HMX when an aliquot was boiled with 70% nitric acid. The main bulk was centrifuged in aqueous zinc chloride (d. 1.70) and the light fraction crystallized from acetone-ethanol and from nitromethane to yield 1.44 gm. of 1-propanoyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, m.p. 198.5° to 199.5° C. (7% of theory, 1 : 1 mole basis), identified by mixed melting point. The low yield is caused by wasteful crystallization which did, however, establish the absence of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane among the reaction products.

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THE HALF LIFE OF C^{14} ¹

BY R. C. HAWKINGS, R. F. HUNTER, W. B. MANN, AND W. H. STEVENS

Abstract

Compensated gas counters of known efficiency, filled with carbon disulphide and carbon dioxide containing a mass-spectrometrically determined proportion of $C^{14}O_2$, have been used to determine the half life of C^{14} . The half life has been found to be 6360 ± 200 years.

Introduction

Within the last two years experiments to determine the half-life of C^{14} have been reported by Reid, Dunning, Weinhouse, and Grosse (10) and by Norris and Inghram (7, 8). The former authors obtained a value of 4700 years, and the latter, values of 6100, 5300, and 5100 years. The value of 5100 years obtained by Norris and Inghram (8) supersedes those previously obtained by the same authors (7).

To determine the half life of a long-lived radioactive isotope of an element such as C^{14} , the values of dN/dt and N in the relation $dN/dt = -\lambda N$ must be measured. In the experiments referred to above, the disintegration rate, dN/dt , was measured using an end-window type of Geiger-Müller counter and the number of C^{14} atoms, N , present at time t , was determined by means of a mass spectrometer.

The use of an end-window type of Geiger-Müller counter with an external source for the absolute measurement of radioactive disintegration rates is always open to some doubt, even with sources emitting energetic beta particles, owing to the corrections that have to be made for absorption, including self-absorption, and back-scattering. In the case of a low energy beta particle emitter, such as C^{14} , these corrections become more important and the value obtained for the disintegration rate becomes more uncertain.

The uncertainties due to absorption and back-scattering are eliminated by the use of a gas counter of the type described by Miller (1, 6). To provide C^{14} standards for this project, use was made of such gas counters to determine the absolute disintegration rate. Absolute measurements of the disintegration rate of C^{14} , in the form of carbon dioxide, can be made provided the internal efficiencies of these counters are known. Extensive experiments have been carried out to determine the internal efficiency of a Miller type gas counter.* From the results of these experiments, together with a mass spectrometric determination of N , a new value for the half life of C^{14} has been obtained.

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* See succeeding paper.

Production of C^{14}

To produce significant quantities of high specific activity C^{14} , a rather large amount of a suitable nitrogen-containing compound must be irradiated in a high thermal neutron flux for a considerable time. The C^{14} which is formed from the nuclear transformation $N^{14}(n, p)C^{14}$ must then be extracted. Methods for production of C^{14} from neutron irradiated ammonium nitrate solution and beryllium nitride have been reported in the literature (9, 12). From considerations of stability, undesirable nuclear reactions on irradiation, purity, and ease of extraction, solid potassium nitrate has been selected as the most suitable compound for irradiation in the Chalk River pile for the production of C^{14} .

Reagent grade potassium nitrate was melted in a stainless steel pot and cast into rods 6 in. long and 1.25 in. in diameter, using a stainless steel mold. These rods were slid into a long aluminum cylinder, which was sealed and which then served as the irradiation container. This material was then exposed to a total thermal neutron irradiation of approximately 2×10^{19} neutrons per sq. cm.

The C^{14} produced in the potassium nitrate under these conditions appears to be present entirely as carbonate ion or as carbon dioxide trapped in the crystal structure, since carbon dioxide is the only active carbon compound it has been possible to obtain from the irradiated potassium nitrate. This could be expected from theoretical considerations such as those discussed by Libby (3). During irradiation the potassium nitrate also decomposed into nitrite and oxygen to a slight extent. To extract the C^{14} , the irradiated potassium nitrate rods were dissolved in 1 *N* nitric acid containing 5% by weight of hydrogen peroxide. This solution oxidizes the small amount of nitrite ion and almost completely prevents the formation of nitrogen dioxide. The oxygen and carbon dioxide were swept into carbonate-free sodium hydroxide solution (2) with carbon-dioxide-free air. Barium carbonate was then precipitated by the addition of barium chloride solution and the solid barium carbonate washed with boiled distilled water. To obtain a purer, more uniform source of C^{14} , carbon dioxide was regenerated from the barium carbonate with boiled dilute nitric acid and reabsorbed in 0.5 *N* carbonate-free sodium hydroxide. Precautions were taken at all times to prevent contamination with inactive carbonate and included carrying out extraction operations in carbon-dioxide-free air or in nitrogen. The 0.5 *N* sodium hydroxide solution was used as the source of C^{14} .

Preparation of Carbon Dioxide Sample

In view of the different amounts of C^{14} required for the mass-spectrometric and counting experiments the carbon dioxide samples for each had to be prepared separately, the C^{14} content for the latter experiments having to be accurately diluted by a factor of the order of 10^5 .

Samples of carbon dioxide for the determination of the absolute disintegration rate were prepared in the following manner. An aliquot of the 0.5 *N* sodium hydroxide solution of C^{14} was diluted to a known volume with a solution of sodium carbonate carrier of known strength. An aliquot of this diluted solution was transferred to a long narrow Pyrex test tube containing a weighed amount of anhydrous sodium carbonate (0.5 gm.) and the tube shaken until the carbonate dissolved. By this method of dilution isotopic homogeneity is assured. A small quantity of carbonate-free sodium hydroxide solution was added to maintain a pH greater than 10. The solution was then evaporated and dried at 140° C. Carbon dioxide was generated from the residue by ignition with excess lead chloride and the resulting carbon dioxide collected in a sample tube by freezing with liquid nitrogen. Three such samples were prepared.

The carbon dioxide for the mass-spectrometric determination of the abundance of C^{14} was prepared as follows. Two aliquots of the 0.5 *N* sodium hydroxide solution containing C^{14} as sodium carbonate were taken. The C^{14} in each was precipitated as barium carbonate by the addition of barium chloride. The barium carbonate was separated by centrifuging, carefully washed with water and ethyl alcohol,* and dried at 140° C. After weighing, the precipitate was again dried at 240° C. and reweighed. Any C^{14} remaining in the combined supernatant liquid and wash solutions for each aliquot was recovered by addition of carbonate carrier as sodium carbonate followed by washing, drying, and weighing as before. The samples were then transferred to a vacuum system for conversion to carbon dioxide. The two precipitates from the original solutions were outgassed at 200° C. and converted to carbon dioxide (samples 4a and 5a, Table III) by ignition in a quartz tube at 1000° to 1200° C. Ignition was continued until no further carbon dioxide was evolved. All the carbon dioxide was collected by freezing with liquid nitrogen. The precipitates from the combined supernatant and wash solutions were separately converted to carbon dioxide (samples 4b and 5b, Table III) by ignition in a Pyrex tube with approximately five molecular proportions of carbonate-free lead chloride.† Such a mixture forms a liquid melt that rapidly evolves carbon dioxide at about 350° C.

The Counting Equipment

The gas counters used were of the compensated type that have already been described (5). These counters were designed to eliminate end errors due to field distortion and to beta particles entering the counting volume from the space outside the cathode. The units used were of extremely simple design, being assembled from copper tubing and glass spacers in the manner indicated in Fig. 1. Two sets of such counters were used, one set consisting

* It should be noted that the molecular structure of ethyl alcohol is such as to preclude the exchange of carbon atoms with the barium carbonate.

† The use of lead chloride for the conversion of barium carbonate to carbon dioxide was suggested in a private communication from F. T. Bonner and S. O. Thompson, Brookhaven National Laboratory, through L. Yaffe, National Research Council, Chalk River, Ontario.

of a long and a short cathode of 1.167 cm. diameter and the second set having cathodes of 1.384 cm. diameter. In each compensated unit of two counters the long cathode was 6 in. long and the short cathode was 2 in. long. The geometries of the ends of the long and short counters of each unit should, in order to eliminate end effects, be constructed similarly and this, with the design illustrated in Fig. 1, is readily accomplished.*

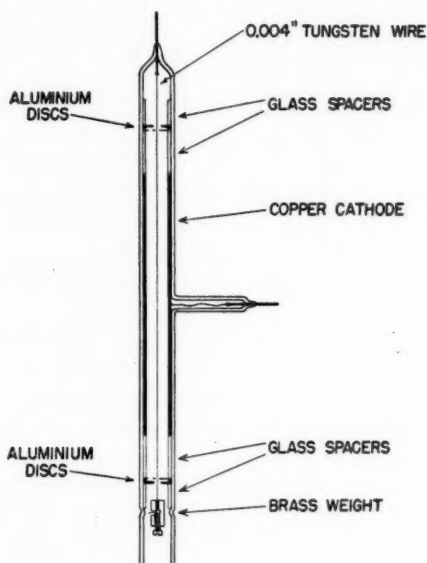


FIG. 1. Section through gas counter tube.

Measurements were carried out with these counters using filling mixtures of about 20 cm. of mercury pressure of carbon dioxide and a little under 1 cm. of mercury pressure of carbon disulphide. Such mixtures are nonselfquenching so that it was necessary to use external quenching, provided in the form of a Parkinson multivibrator quenching unit (5). The high voltage for these counters was provided by a stabilized 4000 v. power unit, type 200†, and the number of counts was registered by means of a Dynatron scale-of-a-hundred

* Instead of using separate long and short units a more convenient form of such a counter could be constructed in the manner indicated in Fig. 1 but with the two cathodes in the same glass tube. Such a counter would be assembled as follows (proceeding from the top down): glass tube; two aluminum disks as in Fig. 1; 1-in. long glass spacer; long (6 in.) cathode; 1-in. long glass spacer; thin aluminum disk, with 1/64 in. hole, to center the wire and to separate counter volumes; 1-in. long glass spacer; short (2 in.) cathode; 1-in. long glass spacer; two aluminum disks as at bottom of Fig. 1. The same 0.004 in. tungsten wire would then be stretched through both counters.

† These are T.R.E. designed instruments assigned these type numbers by the U.K. Ministry of Supply. The model used was manufactured by Dynatron Radio Ltd., of Maidenhead, England. The units are voltage stabilized to $\pm 2\%$ of maximum voltage on any range and input regulation such that $\pm 10\%$ variation in line voltage produces variation in output voltage of not more than $\pm 0.56\%$.

scaling unit, type 200. A quench time of about 400 $\mu\text{sec.}$ was found to give satisfactory plateaux.

The filling of the counters was carried out by means of a vacuum system and the counters were isolated from the rest of the system by means of mercury valves. The pressure of gas in the system was measured by means of a mercury U-tube manometer made from glass tubing of 1 cm. bore, the readings of which could be made reproducibly to 0.01 cm. using a cathetometer. The transfer of carbon dioxide or carbon disulphide from one part of the vacuum system to another was accomplished by freezing in liquid nitrogen.

Subsidiary experiments have been carried out using a compensated counting unit having cathodes 18 in. and 14.5 in. long and 3 in. in diameter in order to determine the efficiency of such gas counters. For additional confirmation, readings at different gas pressures were also obtained. The results of these and other experiments, which were extensive in nature and which were designed to check the efficiencies of the counters, will be published separately, but strong evidence has been obtained to prove that these counters do in fact have an efficiency that is not significantly less than 100%.

Disintegration Rates

Measurements were made on three samples of carbon dioxide containing C^{14} . The results obtained with one of these samples (Sample 1) are shown in Fig. 2 in which the plateaux are plotted for each of the four counters.

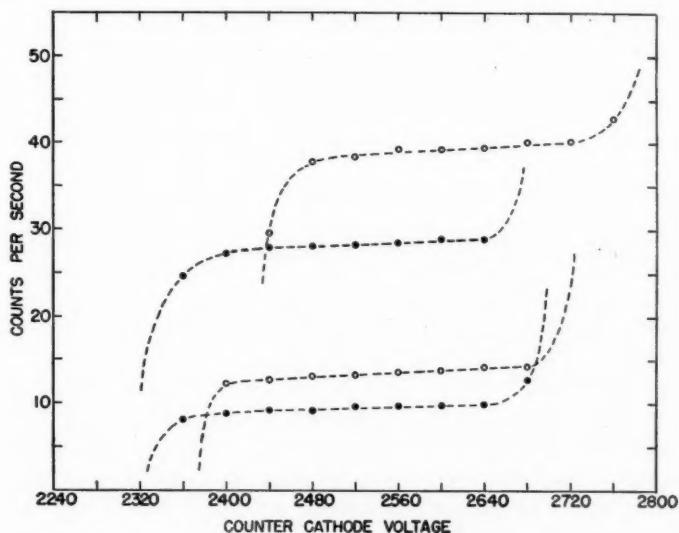


FIG. 2. Plateaux for narrow and wide compensated counting units. Solid circles show results for short and long 1.167 cm. counters; open circles results for short and long 1.384 cm. counters. Pressure of carbon dioxide is 19.36 cm. of mercury at 25° C. and that of carbon disulphide is 0.89 cm. of mercury at 25° C.

It will be observed that none of the plateaux shown in Fig. 2 are completely flat. This appears to be due to the attenuation of the electric field at each end of the counting volume. As the cathode is made more negative so will the electric intensity at the ends of the anode wire be increased, and the effective counting volume be extended to fill a greater proportion of the cathode volume. If the end geometries for both the short and long counters are similar, then the variation of field at the ends of the cathodes with changing cathode voltage will also be similar. The increase in counts due to this effect, with increasing voltage across the counter, should therefore be the same for both the long and short counters of either unit, and the difference in the counting rates of the long and short counters of a unit (taken at the same voltage) should remain constant with increasing voltage in the Geiger region.

In Table I this differential count for different cathode voltages is shown for both the narrow and wide counter units. These results are obtained from

TABLE I

Cathode volts (negative)	Wide counter unit (counts per second)			Narrow counter unit (counts per second)		
	Long counter	Short counter	Differential count	Long counter	Short counter	Differential count
2400		12.20		27.30 ± 0.19	8.75 ± 0.09	18.55 ± 0.21
2440	29.62	12.66		28.00	9.22	18.78
2480	37.88 ± 0.25	13.02 ± 0.08	24.86 ± 0.26	28.10	9.08	18.02
2520	38.48	13.24	25.24	28.42	9.61	18.81
2560	39.28	13.54	25.74	28.61	9.74	18.87
2600	39.29	13.84	25.45	29.01	9.84	19.17
2640	39.48	14.16	25.32	29.02	9.91	19.11
2680	40.11	14.28	25.83		12.77	
2720	40.24	14.84	25.40			
2760	42.95	—				
2790	—					

the same data as were used to plot the plateaux of Fig. 2. It will be seen that within the limits of experimental error the differential count is constant with increasing counter voltage. The differential volume, i.e., the difference in volume between the long and short cathode volumes, is equal to 15.09 cm^3 for the wide counters and 10.79 cm^3 for the narrow counter unit. The differential volume of 15.09 cm^3 is thus seen, from Table I, to give rise to 25.41 ± 0.10 counts per second while the differential volume of 10.79 cm^3 corresponds to 18.76 ± 0.08 counts per second. Errors shown are probable errors based on the total number of counts taken. The counts per second per unit volume of Sample 1 at the pressure of the experiment are therefore 1.68 ± 0.01 and 1.74 ± 0.01 , respectively, for the wide and narrow counting units. The agreement between these results for counters of different radii shows that errors arising from the loss of counts at the cathode walls are either small or completely absent.

Similar measurements were carried out on Samples 2 and 3, with the results shown in Table II. The dead time of the quenching circuit was increased to 4.2 milliseconds for the measurements on Sample 3. The errors shown in Table II are also probable errors.

TABLE II

Sample	Gas pressure* in counter (cm. Hg at 25° C.)		Differential counts per sec. per cm. ³		Average counts per sec. $\times 10^{-6}$ per ml. of 0.5 N NaOH solution of $Na_2C^{14}O_3$
	CO ₂	CS ₂	1.167 cm. diam. counters	1.384 cm. diam. counters	
1	19.36	0.89	1.738 ± 0.009	1.684 ± 0.011	1.62 ± 0.03
2	20.04	0.52	0.868 ± 0.015	0.860 ± 0.014	1.57 ± 0.03
3	14.53	1.03	1.298 ± 0.007	1.257 ± 0.007	1.61 ± 0.03

* Pressures corrected from temperature inside lead castle to 25° C.

Mass Spectrometric Analysis

The carbon dioxide was analyzed in a 180° Nier type mass spectrometer. The ion beams were scanned by automatic variation of the magnetic field and the intensities corresponding to masses 44, 45, and 46 automatically recorded (4, 11). The intensity of the mass-48 ion beam was not recorded because of uncertainties in the background for this mass. A typical recorder tracing for a normal carbon dioxide sample and for one containing C^{14} in approximately 6.2% abundance are shown in Figs. 3 and 4.

The results of the mass-spectrometric analyses are given in Table III.

TABLE III
ISOTOPIC ABUNDANCE RATIOS AND PERCENTAGES

Sample	Ratio $\frac{\text{Mass 44}}{\text{Mass 46}}$	Ratio $\frac{\text{Mass 44}}{\text{Mass 45}}$	Per cent C^{14} ***	Per cent C^{14} corrected
4a (1st precipitation)	14.29 ± 0.02	85.86 ± 0.02	6.08 ± 0.01	6.10
4b (2nd precipitation)	228.2 ± 0.7	85.33 ± 0.04	0.013 ± 0.002	0.01 ₃
5a (1st precipitation)	13.91 ± 0.01	85.91 ± 0.01	6.24 ± 0.01	6.27
5b (2nd precipitation)	213.6 ± 0.2	85.84 ± 0.02	0.043 ± 0.001	0.04 ₃
Normal CO ₂ A*	235.6 ± 0.3	85.67 ± 0.06	—	—
B**	236.2 ± 0.40	85.67 ± 0.03	—	—

* In equilibrium with Lake Ontario water.

** In equilibrium with Ottawa River water.

*** Not corrected for mass-48 contribution.

The method of preparation of the samples was such that the oxygen of mass 18 should be in equilibrium with oxygen from the water of the Ottawa River. The contribution of oxygen 18 to the mass-46 peak would, therefore,

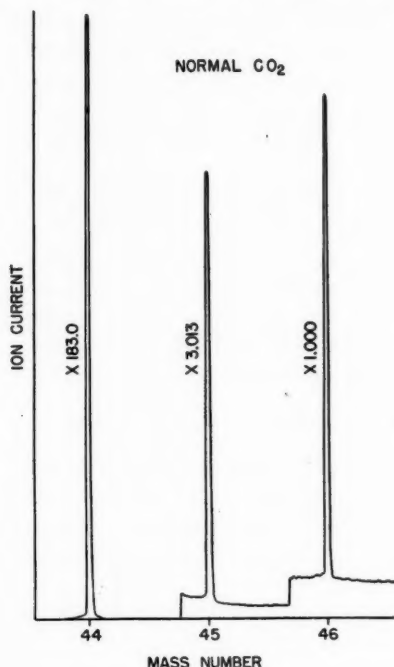


FIG. 3. Mass-spectrometer recorder tracing. Shunt factors are shown alongside each peak.

be the same as for normal carbon dioxide. The contribution of C^{13} to mass 46 is negligible since it depends upon the low abundance of O^{17} . The fact that the ratio of mass 44 to mass 45 (i.e., of C^{12} to C^{13} , neglecting the $C^{12}O^{16}O^{17}$ contribution of 0.08%) remains constant for both the inactive and C^{14} -enriched samples (Table III) means that the C^{12} and C^{13} in the enriched sample arise from carbonate impurity in the reagents used in the production of C^{14} ; no significant amount of C^{13} can have been produced by neutron capture by C^{12} . This is also borne out by the known low neutron capture cross section of C^{12} . This correction has been made with sufficient accuracy by calculation, using the known O^{18} abundance for the normal sample and the approximate percentage of C^{14} . The C^{14} percentages corrected in this manner are given in the last column of Table III.

The values of N , the number of C^{14} atoms per milliliter of original solution, as calculated from the mass-spectrometer data and the weights of the precipitates, are shown in Table IV.

The difference in the per cent C^{14} obtained for the first precipitation on each sample may be due to fractionation of the carbon isotopes during the precipitation as barium carbonate. The possibility that the difference can be due to absorption of atmospheric carbon dioxide by the solution is considered unlikely on the basis of the experimental conditions, the separations having been carried out in an atmosphere of nitrogen. It is even more

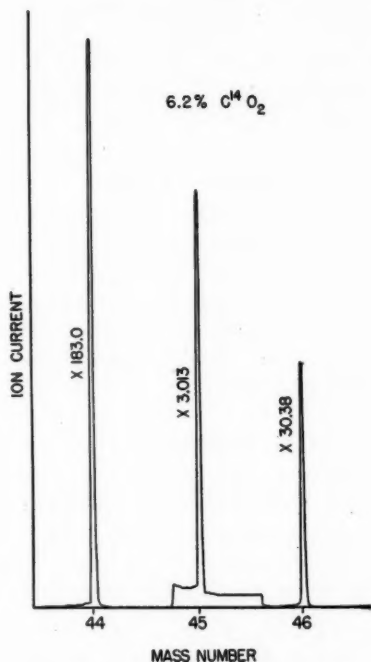


FIG. 4. Mass-spectrometer recorder tracing. Shunt factors are shown alongside each peak. It should be noted that the sensitivity for mass 46 is about one-thirtieth of that for mass 44 in Fig. 3.

TABLE IV

C^{14} ATOMS PER MILLILITER OF ORIGINAL 0.5 N
SODIUM HYDROXIDE SOLUTION OF C^{14}

Sample	N
4a + 4b	$4.76 \pm 0.03 \times 10^{17}$
5a + 5b	$4.77 \pm 0.03 \times 10^{17}$

unlikely that C^{14} could have been lost from either sample. The agreement in the final values obtained for the number of C^{14} atoms per milliliter of original solution supports the possibility of isotopic fractionation.

The Half life of C^{14}

On substituting the mean value of dN/dt equal to 1.60×10^6 disintegrations per second, from Table II, and the mean values of N equal to 4.77×10^{17} atoms of C^{14} , from Table IV, into the relation $dN/dt = \lambda N$, a value for λ of 3.35×10^{-12} sec.⁻¹ is obtained. This corresponds to a half-life of 2.07×10^{11} sec. or 6560 ± 200 years.

The results obtained with the 6.998 cm. diameter counters would, if used to calculate the half life of C^{14} , be in very close agreement with those obtained with the 1.167 cm. diameter counters (see Table II of succeeding paper).

The efficiency of the 1.167 cm. diameter counters has been found to be about 97% (see succeeding paper). This efficiency gives a half life for C^{14} of 6360 ± 200 years.

Acknowledgments

We wish to thank Prof. H. G. Thode, of McMaster University, for placing at our disposal the facilities of his laboratory and gratefully to acknowledge the assistance of Mr. C. Collins, who operated the mass spectrometer. We also wish to thank Mr. G. B. Parkinson for assistance with the counting equipment and Mr. F. N. MacGillivray who constructed the quenching unit and helped in many other ways. Thanks are also due to Mr. N. Jupe who assisted in the separation of the C^{14} .

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ON THE EFFICIENCY OF GAS COUNTERS FILLED WITH CARBON DIOXIDE AND CARBON DISULPHIDE¹

R. C. HAWKINGS, R. F. HUNTER, AND W. B. MANN

Abstract

The efficiencies of compensated gas counters filled with carbon dioxide and carbon disulphide have been investigated for the purpose of determining absolute disintegration rates of $C^{14}O_2$ samples. In addition to comparing compensated counting units of different radii, a special counter has been constructed to determine the efficiency at different radii using a collimated beam of electrons from Tl^{204} . The carbon dioxide and carbon disulphide filled counters have been shown to be at least 97% efficient.

Introduction

Measurements that have been made to determine absolute activities of C^1 in samples of carbon dioxide using gas counters have necessitated a very extensive investigation into the internal efficiencies of such counters.

In using such counters it is necessary to take into consideration two possible sources of error, namely, that due to end effects and that due to the possibility of C^{14} disintegrations near the counter walls giving rise to beta particles that enter the wall without creating enough ion pairs to register a count.

It is the purpose of this paper to give a brief description of the conditions under which such counters can be used to give reliable quantitative measurements.

The Filling Mixtures

The counting equipment is the same as that which has been previously described consisting of a stabilized negative (or positive) 4000 v. H.T. set, Parkinson quencher (4), and scale-of-one-hundred scaler.

To determine the best mixtures of carbon dioxide and carbon disulphide with which to fill the counters preliminary experiments were carried out with a single 0.5 in. diameter platinum tube counter having a 0.004 in. diameter tungsten wire anode. With this counter it was found that plateaux could be obtained with any mixture of the two gases varying from practically 100% carbon dioxide to 100% carbon disulphide. The results that were obtained using these gases undiluted and also a mixture of 50% carbon dioxide and 50% carbon disulphide are shown in Fig. 1.

While the results for carbon dioxide are given as nominally for undiluted gas they were obtained after the counters had been used for a carbon dioxide and carbon disulphide mixture. After pumping out this mixture pure carbon dioxide was admitted but it is felt that a trace of carbon disulphide was probably present since, after further and very extended pumping, plateaux

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could not be obtained with pure carbon dioxide. The different plateaux shown in Fig. 1 for each mixture are for different quench times Q of the quenching equipment.

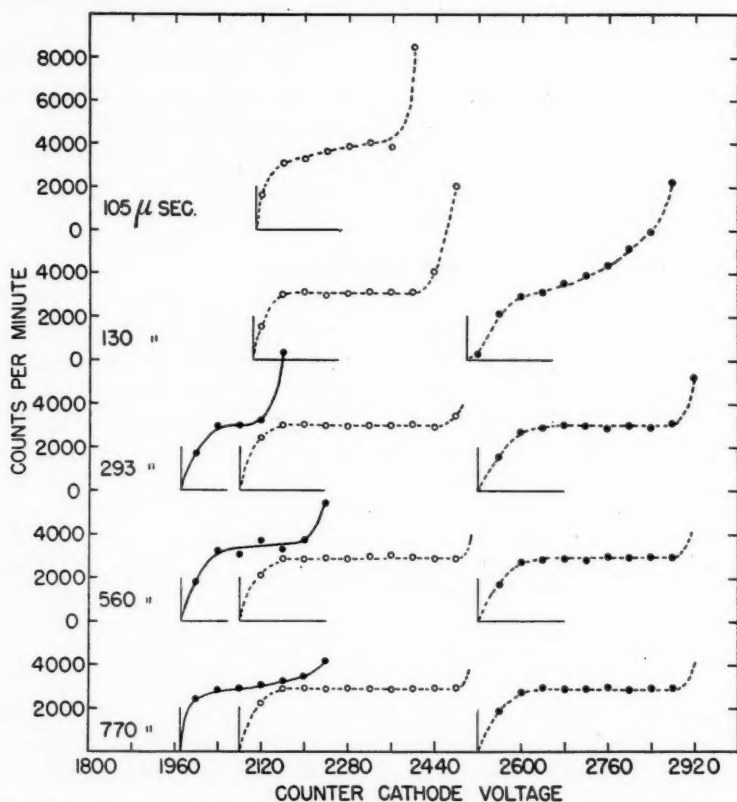


FIG. 1. Effect of varying proportions of carbon dioxide and carbon disulphide. Solid circles represent "pure" carbon dioxide (left) and pure carbon disulphide (right). Open circles represent 50% carbon dioxide mixed with 50% carbon disulphide. The total pressure in every case was about 10 cm. of mercury. The quench period of the external quenching circuit was varied from 105 to 770 μ sec. and that corresponding to each set of curves is shown on the left; all curves on the same horizontal have the same quench period.

For most practical purposes it is necessary to use fillings that shall be predominantly carbon dioxide since the active C^{14} can be more readily converted into carbon dioxide than into carbon disulphide. It is seen from Fig. 1, that "pure" carbon dioxide (with much less than 0.001 cm. of mercury pressure of carbon disulphide) gives plateaux that are a little shorter than is desirable for accurate and reproducible measurements. The addition of approximately only 0.001 cm. of mercury of carbon disulphide serves to give excellent plateaux as shown in Fig. 2. The pressures of carbon dioxide for Curves (a),

(b), (c), and (d) are approximately 5, 10, 15, and 20 cm. of mercury, respectively; thus for most practical purposes the small pressure of carbon disulphide can be neglected. At 20 cm. of mercury pressure instability

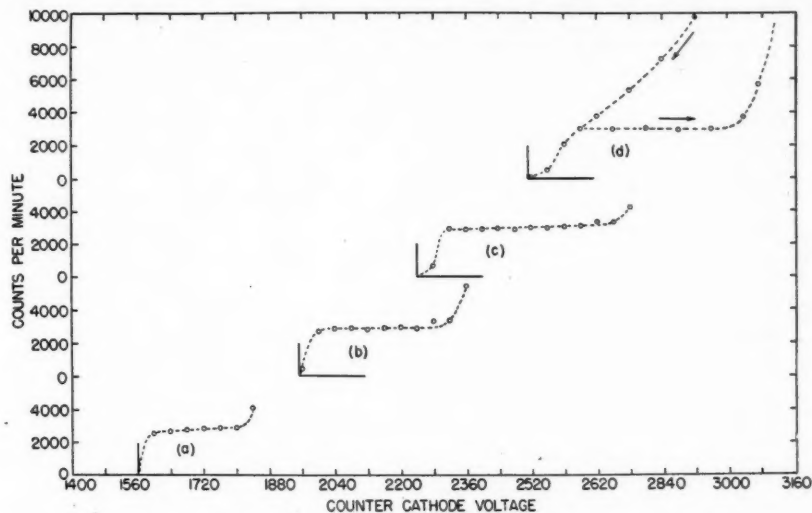


FIG. 2. Plateaux with carbon dioxide fillings mixed with carbon disulphide at 0.001 cm. of mercury pressure. Pressure of carbon disulphide approximately (a) 5, (b) 10, (c) 15, and (d) 20 cm. of mercury. Alternate points on each curve were obtained with increasing and decreasing values of the applied voltage. Curve (d) shows instability in that after exceeding the plateau or increasing voltage the counts do not fall to the plateau again until the voltage is substantially reduced.

became apparent. This was removed, however, by increasing the pressure of carbon disulphide to 0.01 cm. of mercury (Fig. 3).

The effect on threshold voltage obtained by varying the relative proportions of carbon dioxide and carbon disulphide is shown in Fig. 4. The curve for carbon dioxide at 20 cm. of mercury is in agreement with the curve shown by Brown and Miller (1) for carbon dioxide at the same pressure.

The End Correction

Brown and Miller found that, for counters of different length, the counting rate multiplied by V_T/V_C , where V_T was the total counter volume and V_C the cathode volume, was proportional to the number of gram molecules of carbon dioxide, containing a fixed proportion of active carbon dioxide. This would seem to imply that their end correction was small or insignificant.

In the present experiments compensated counter units (4) have been used. If L be the length of the long counter and l that of the short counter comprising the unit, then the difference in counting rates for the long and short counters, when they are filled with the same mixture of active gas, divided by $L - l$

should give the counting rate per unit length for an "ideal" or infinitely long counter.

If this "ideal" counting rate per unit length be multiplied by L , then the difference from the observed count for the long counter will give the end

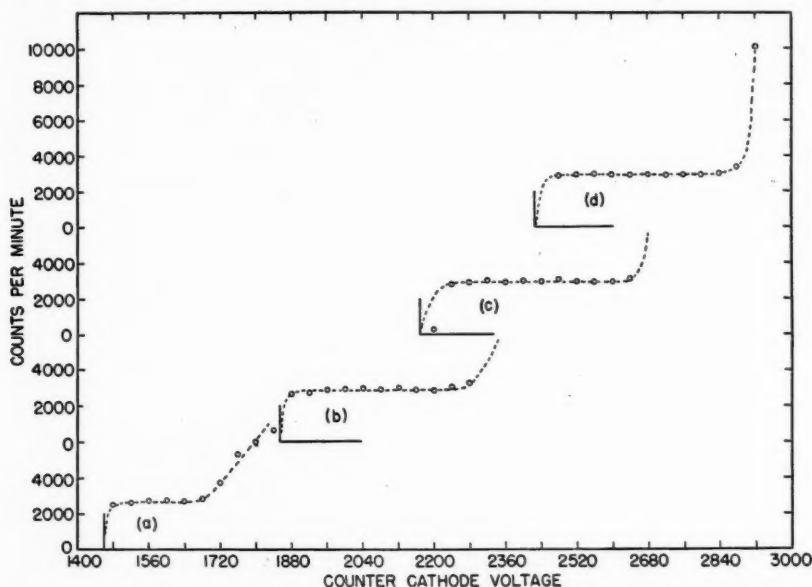


FIG. 3. Plateaux with carbon dioxide fillings mixed with carbon disulphide at 0.01 cm. of mercury pressure. Pressure of carbon dioxide approximately (a) 5, (b) 10, (c) 15, and (d) 20 cm. of mercury. Alternate points on each curve were obtained with increasing and decreasing values of the applied voltage.

correction directly. The same may be done for the short counter and if compensation has been achieved the end effect should be the same in each case. Typical results obtained on doing this for counters of different lengths and radii are shown in Table I. It should be noted that all counters were

TABLE I

Counter radius, cm.	Counter length, cm.	Counts per sec.	"Ideal" counts, N/sec./cm.	Length \times N, counts/sec.	End corrections, counts/sec.
3.499	45.65	53.6	1.313	59.9	6.3
3.499	36.74	41.9		48.2	6.3
0.697	15.22	19.74	1.292	19.70	-0.04
0.697	5.19	6.77		6.72	-0.05

constructed with a 1 in. glass spacer between the cathode and the aluminum disk which centered the anode wire at each end. In other words the end volumes extend 1 in. beyond the cathode in all counters.

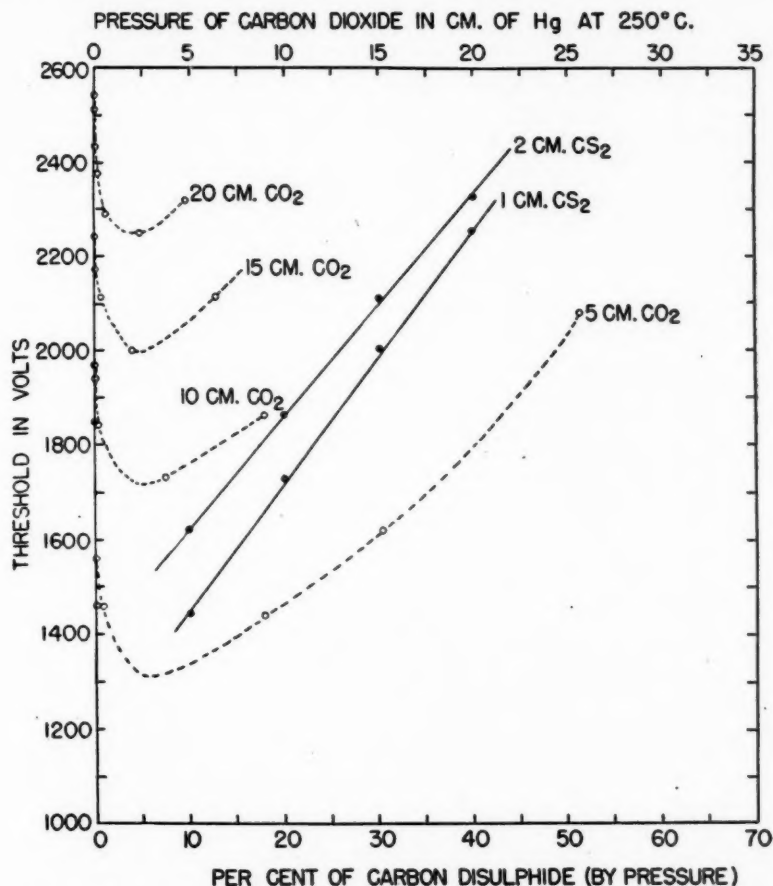


FIG. 4. Threshold voltages for different mixtures of carbon dioxide and carbon disulphide. The lower abscissae refer to the dotted curves for constant pressures of carbon dioxide. The upper abscissae refer to the solid curves for constant pressures of carbon disulphide.

The change in sign of the end correction, shown in Table I, is interesting and indicates that under certain circumstances the end correction for a small diameter counter may be zero.

The end correction will be comprised of two parts, namely, a negative correction for particles entering the active counting volume from the "dead" volume at each end and a positive correction for counts lost by the attenuation of the electric field at each end of the cathode.

With a large diameter counter the positive correction due to field distortion would be expected to be greater than that for particles entering the end. On the other hand, when one increases the applied voltage and moves along the plateau the electric field at the cathode ends increases and the active volume increases. The counting rate will increase and the positive correction that has to be made because of losses inside the cathode volume at each end decreases. At some point the positive and negative corrections may be equal; such a condition seems to have been attained with the compensated counting unit of small diameter in Table I. It would also seem that Brown and Miller have used a point on their plateau that appears to have effected such a compromise. In general, however, it is probably more definite to eliminate the end correction entirely by using compensated counters.

The Radius Correction

It is possible that a C^{14} nucleus disintegrating near the cathode may project a beta particle towards the cathode wall and that it may enter the cathode without initiating an electron avalanche. Assuming a pressure of carbon dioxide of about 20 cm. of mercury it is possible to calculate the probable order of magnitude of this effect.

The average energy of the C^{14} beta particles is about 50,000 v., i.e., about one-third the maximum energy. This energy corresponds approximately to an ion-pair formation of 200 per cm. path in air at N.T.P. (5). A number of authors (2, 3, 6)* have shown that the ionization produced in carbon dioxide by alpha particles is not very different from that produced in air. It has been assumed therefore that the same will also be true for beta particles, at least to the degree of accuracy required in this approximate calculation.

The equivalent ion-pair formation in carbon dioxide by a C^{14} beta particle at 20 cm. of mercury pressure will, therefore, be of the order of 50 per cm. or one ion pair per 0.2 mm. of path. Thus less than half of the C^{14} nuclei disintegrating within approximately 0.2 mm. of the cathode will not give rise to counts. In a counter with a 0.5 in. diameter this gives a count that is too low by not more than 6.5% while the corresponding error for a 3 in. diameter cathode is only 1%.

To demonstrate that the inefficiency of the counters due to this radius effect was not greater than the calculated value the large diameter compensated counting unit already referred to in Table I was assembled. A photograph of two such counters is shown in Fig. 5. The dimensions of the counters used are given in Table I.†

* We are indebted to Mr. J. Dainty for drawing our attention to the work of these authors.

† To obtain satisfactory plateaux with these counters it was necessary to increase the quench period Q of the Parkinson quencher to 4 or 5 milliseconds. This was achieved by increasing C_1 to 0.003 and C_2 to 0.01 μ f. (4).

For lower quench periods the 6.998 cm. diameter counters gave a very high count for an applied voltage only a little above the threshold. This then dropped to a normal counting rate and gave a normal plateau on increasing the voltage. This peak at the low voltage end of the plateau is probably due to the fact that the positive ion sheath does not quite reach the cathode before the voltage is applied again after the quench period. This peak disappeared on increasing the quench period to about 4.2 milliseconds.

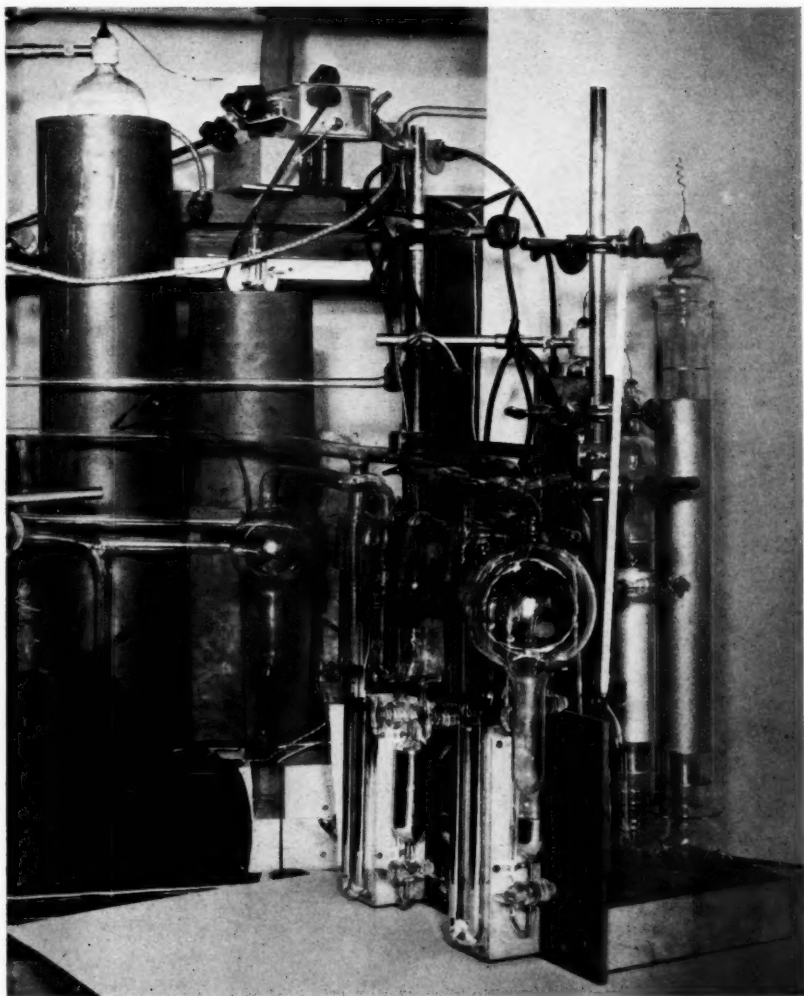
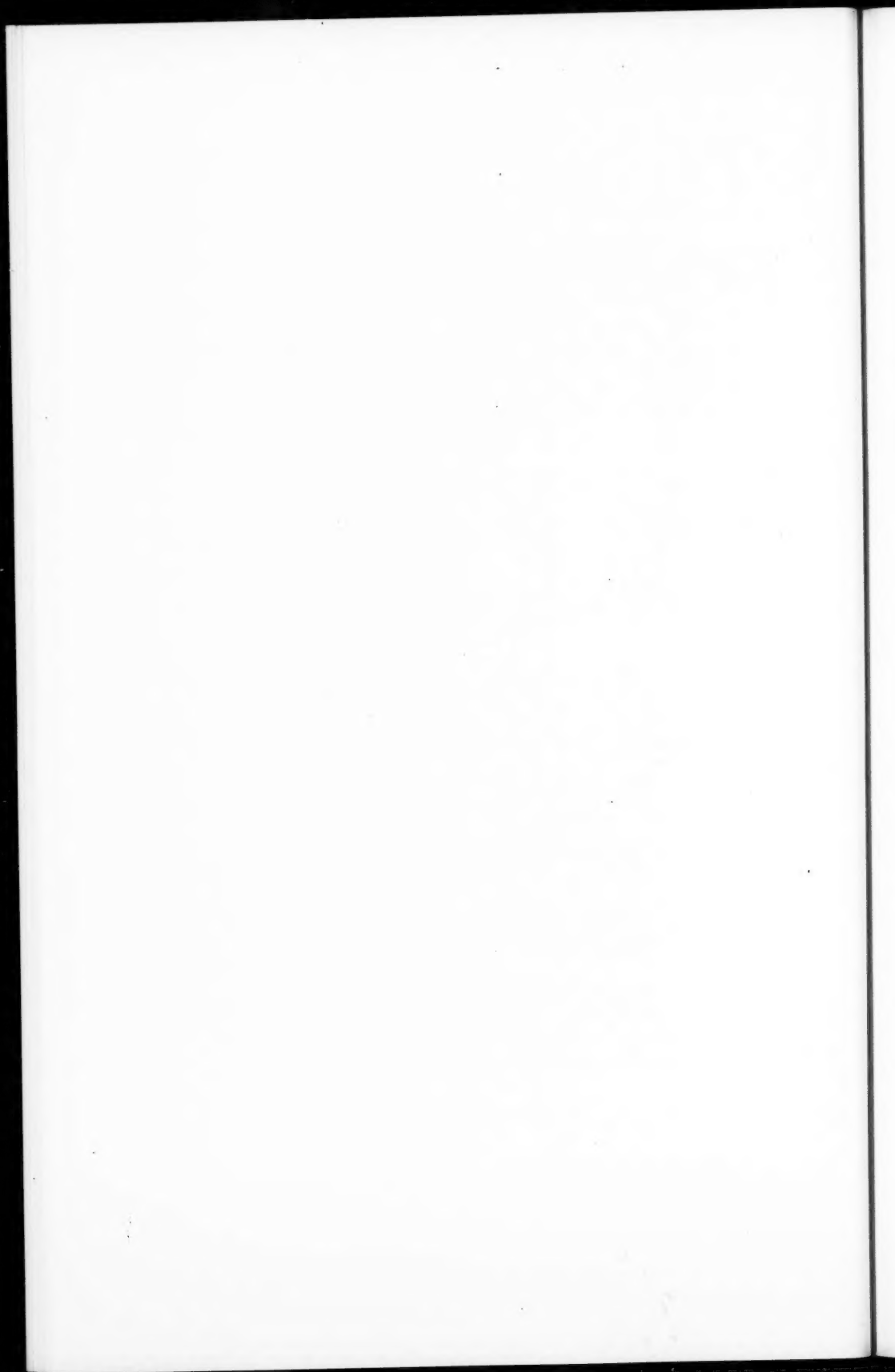


FIG. 5. *The two unshielded counters seen on the right comprise a set of 1½ in. diameter counters. The long and short 3 in. diameter counters are on the left and are shielded by lead.*



To prove that the error due to any radius effect is less than that estimated above it is necessary to show that the counts per unit (cathode) volume in counters of approximately 0.5 in. and 3 in. diameter is not greatly different. On the basis of the rough calculation above, a difference of less than 5% should emerge if counts are lost only in a distance less than 0.2 mm. from the cathode.

An experiment was therefore carried out in which carbon dioxide containing C^{14} was admitted to the four small counters used in the determination of the half life of C^{14} .** The counts per unit volume in each of the two sets of compensated counters was determined and the pressure was noted. The results are shown in Table II. Owing to the fact that the volume of the 3-in. counters is considerably greater than that of the smaller counter units it was then necessary to expand a known fraction of the gas from the smaller to the larger counters in order to give a convenient counting rate. Inactive gas was then added to give a suitable total pressure. The complete results are shown in Table II.

TABLE II

Counter radius, cm.	Pressure of original active gas sample, cm. of Hg at 25° C.	Counts per unit volume, sec. ⁻¹ cm. ⁻³	Counts per unit volume corrected to 20 cm. of Hg at 25° C., sec. ⁻¹ cm. ⁻³
0.584	15.555	1.298	1.67
0.697	15.555	1.257	1.62
3.499	0.513	0.0432	1.68

From the results shown in the final column of Table II it is seen that the radius effect is certainly less than that calculated at the beginning of this section and that any correction arising from it is negligible.

A confirmatory experiment was also carried out by approximately doubling the pressure by adding inactive carbon dioxide and carbon disulphide in the long 1.384 cm. diameter counter. The counts with a filling of 10.17 cm. of mercury total pressure was 2.81 counts per second. Inactive gas was added to bring the total pressure up to 19.94 cm. of mercury. The counts observed were 2.82 per second. This is in agreement with the results obtained using external sources and inactive gas fillings. In these it was observed that the counting rate of the plateaux was the same over wide ranges of pressure when the geometry of the external Co^{60} source was unchanged (see Figs. 3 and 4).

Another kind of radius effect could, however, occur if such large counters showed a variation of efficiency as a function of radius due to some inherent property of the gas filling (e.g., loss of counts initiated in regions of low electric intensity remote from the wire). Such an effect should emerge from the experiment described above but an additional experiment was carried out with the apparatus illustrated in Fig. 6. In this apparatus a collimated beam of electrons could be directed into the counter in a direction parallel

** See preceding paper.

to the counter axis at different radii. The source used was Tl^{204} , which was prepared by irradiating a small piece of thallium metal in the pile. The resulting thallium activity was checked and found to have negligibly small

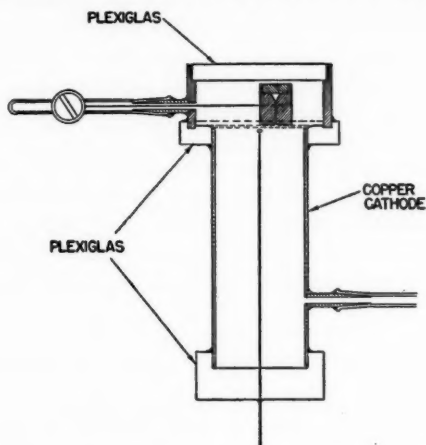


FIG. 6. Section through counter for determining radial efficiency.

gamma ray activity. The maximum energy of the beta particles from Tl^{204} is 1.6 Mev., which is considerably greater than that of those from C^{14} . If, however, there is no change in efficiency with radius using Tl^{204} then there should likewise be none with C^{14} since the specific ionization for the C^{14} beta particles is greater. As will be seen from Fig. 6 the geometry is such that only the beginning of the range of the Tl^{204} beta particles is utilized. The apparatus was designed in such a way as to avoid any kind of window, e.g., mica, so as to eliminate the possibility of spread of the beta particle beam due to scattering. The hole for collimation of the beta particles was 0.8 mm. diameter and 1 in. long. In interpreting the results a small allowance has to be made for the width of the electron beam.

The results obtained using argon at 10 cm. of mercury pressure and ethyl alcohol at 2 cm. of mercury pressure are shown in Fig. 7, in which an indication of the position of anode, anode bead, and cathode is given. Neglecting the extreme dip in the middle caused by absorption of beta particles in the glass bead and integrating for $2\pi Nr.dr$ across the counter an efficiency of 98.4% is obtained. This figure is based on the assumption that the flat part of the curve corresponds to 100% efficiency. This, in turn, is based on the criterion that, in the Geiger region, every particle entering the counter gives a count.

Similar results with the counter filled with carbon dioxide at 4.5 cm. of mercury pressure and carbon disulphide at 0.5 cm. of mercury pressure are included in Fig. 7 and show little over-all difference in efficiency from that for argon and alcohol. The region in the center of the counter gives an essentially

identical efficiency for both fillings. It is concluded therefore that the efficiency for the 6.998 cm. diameter counter is of the order of 98%.

The dotted lines in Fig. 7 indicate the geometry of the 1.167 cm. diameter counter. The thresholds of the 1.167 and 6.998 cm. diameter counters were

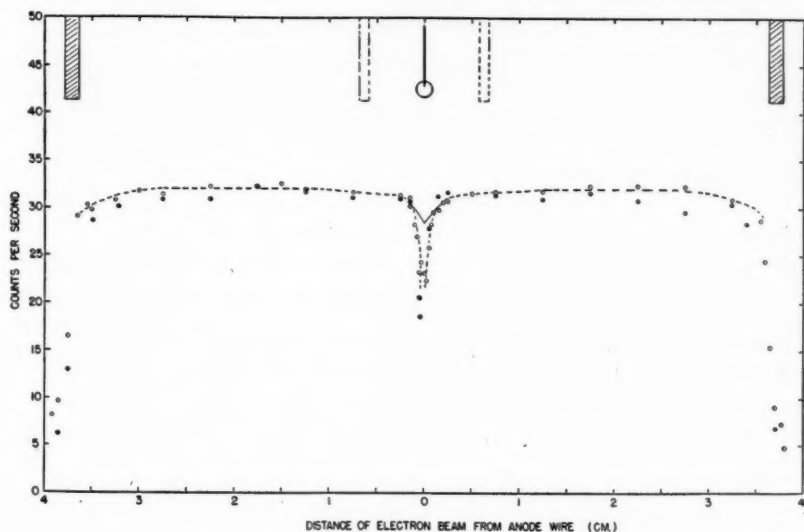


FIG. 7. Change of counting rate with radius. Solid points represent results for carbon dioxide and carbon disulphide. Open circles are results for argon and alcohol.

such as to give approximately the same intensity at the anode wire in each case, namely about 100,000 v. per cm. The distribution of electric intensity across the counter will be the same in both cases, being inversely proportional to radius and independent of cathode radius. It is assumed, therefore, that the variation in efficiency for the 1.167 cm. diameter counter near the anode wire will be the same as that determined for the larger counter. On integrating $2\pi Nr.dr$ up to a radius of 0.584 cm. an efficiency of 96.2% for the 1.167 cm. diameter counter is obtained.

This efficiency, however, is determined with a beam of electrons that is parallel to the anode wire, but in the determination of the C^{14} activity beta particles are emitted uniformly in all directions with an average range of about 9 cm. in carbon dioxide at a pressure of 20 cm. of mercury. The majority of the C^{14} beta particles will, wherever they originate, thus traverse a large region of the counter, creating one ion pair approximately every 0.2 mm. of path and at varying distances from the anode. The efficiency for these particles will therefore lie nearer to the efficiency (98.5%) at the cathode wall and will therefore probably be greater than 96.2%. An average value of 97% has therefore been assumed for the efficiency of the 1.167 cm. diameter counting unit for C^{14} beta particles.

Conclusion

The carbon dioxide and carbon disulphide counters used in the determination of the half life of C^{14} have been shown to be at least 97% efficient and of the same order as that for counters filled with mixtures of argon and alcohol.

Acknowledgments

We wish to thank Dr. W. B. Lewis for his helpful comments on reading this and the preceding paper and Dr. A. J. Cipriani for his ever-ready help in the procurement of equipment and the placing of laboratory and experimental facilities at our disposal. We wish again to thank Mr. F. N. MacGillivray for his assistance.

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THE CARBONYL GROUP IN BIRCH LIGNIN¹

BY ALAN BELL AND GEORGE F WRIGHT

Abstract

When lignin is extracted from birch wood with acetic acid its behavior differs from that of lignin extracted with acetic acid and then boiled with formic acid. There is less hydroxyl lost per methoxyl gained when the lignin treated with formic acid is methylated with diazomethane. An increase in addition of Grignard reagent also corresponds to this increase in methoxyl. This indicates that a lactone linkage is present in extracted lignin but probably not in lignin in the wood, because the effect is less noticeable in lignin more mildly extracted by acetic acid. In dimethyl sulphate - alkali-methylated lignins, where the lactone would no longer be present there is evidence of a carboxyl group which can be diazomethane-methylated and the resulting ester saponified at will.

The addition of Grignard reagent to lignins (about 1 equivalent per kilogram) has shown that a carbonyl group is present (4) in lignin which has been extracted from the wood by formic acid. Comparison of active hydrogen and Grignard reagent addition before and after diazomethane-methylation indicated the possibility that this carbonyl group was part of a lactone linkage (2), especially after it was found that diazomethane contaminated with methanol would react with a lactone (3). Further investigation using acetic acid as an extractant showed that the lactone group was probably not present in the wood, but was formed by the formic acid as a result of glucoside hydrolysis with subsequent lactonization of the resulting carboxyl group (1). In the present report a further evaluation of this hypothesis has been explored by combinations of diazomethane and dimethyl sulphate methylation studies on the lignins extracted from birch wood by both acetic and formic acids.

Reliable evidence has never been presented to show that lignin is a chemical individual, but heterogeneity in birch lignin is especially apparent in the fact that the methoxyl content differs in the several fractions into which it has been separated. Both the ether-soluble and the benzene-soluble fractions have the highest methoxyl content while the fractions soluble only in methanol and chloroform contain less methoxyl. Classification on the basis of methoxyl content of these original fractions is actually not justified because the methanol and chloroform fractions contain considerable carbohydrate. However, removal of the latter from the combined methanol and chloroform-soluble fractions with formic acid (to give acetic-formic lignins) allows separation of this lignin into a fraction soluble only in acetone-water, a fraction which is also soluble in acetone alone, and a fraction which is soluble in chloroform as well. It may be seen in Table I that, after the chemically linked carbohydrate has been removed, the fractions with limited solubility also contain less methoxyl groups than the ether and the benzene-soluble fractions (though they too must contain a small amount of carbohydrate). It may also be

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TABLE I
BIRCH LIGNINS METHYLATED WITH DIAZOMETHANE

Fraction and solubility	Initial OCH_3 , %	Final OCH_3 , %	Yield, wt. %	Grignard analyses in dioxane, per kgm.	
				Act. H	RMgX added
Acetic birch					
Ether	21.0	24.3	80	3.3	1.7
Benzene	20.7	23.1	90	3.5	3.0
Methanol	18.9	23.6	90	2.7	2.4
Chloroform	16.4	21.1	80	2.6	2.4
Acetic-formic birch					
Chloroform	22.1	27.9	90	3.3	2.5
Acetone	19.0	27.6	80	2.9	1.7
Acetone-water	17.8	27.2	80	2.2	2.4

observed that treatment with diazomethane raises the methoxyl values of all three of these acetic-formic fractions to the same level.

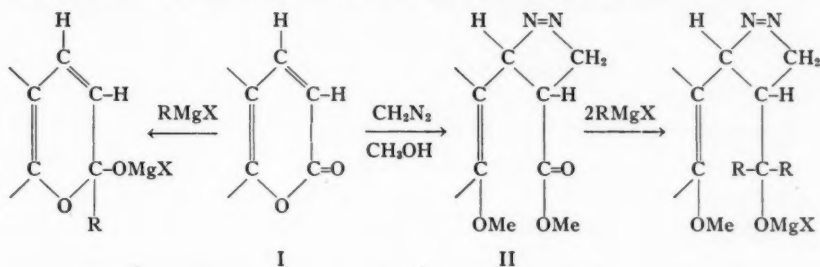
A critical comparison of the methoxyl and Grignard analyses with those for the original fractions has been outlined in Table II. This comparison discloses, first, that the methoxyl increase always is greater than the decrease in active hydrogen as measured in the Grignard machine. This abnormality is recorded in Column 4, Table II, as the difference between Columns 2 and 3.

TABLE II
COMPARISON OF "HYDROXYL LOST" TO "METHOXYL GAINED" IN REACTIONS OF ACETIC AND ACETIC-FORMIC LIGNINS WITH DIAZOMETHANE

(1) Lignin fraction and solubility	(2) Increase OCH_3 /kgm.	(3) Loss, OH/kgm.	(4) Diff. 2-3	(5) Increase addn. RMgX/kgm.
Acetic birch				
Ether	1.2	0.6	0.6	0.8
Benzene	0.8	0.4	0.4	0.85
Methanol	1.7	1.0	0.7	0.65
Chloroform	1.7	0.4	1.3	0.5
Acetic-formic birch				
Chloroform	2.1	0.6	1.5	1.6
Acetone	3.2	0.4	2.8	1.0
Acetone-water	3.4	0.7	2.7	1.4

The table shows, secondly, that this diazomethane methylation causes an enhancement in the amount of Grignard reagent which can be added to the lignin, and this enhancement corresponds very roughly with the increase in methoxyl content (Column 5).

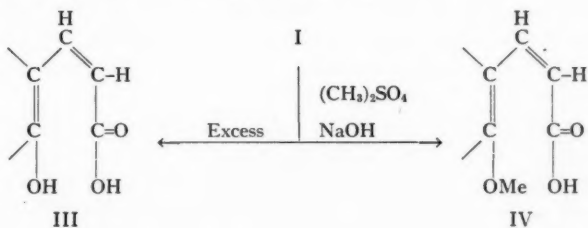
These results may be explained by the assumption that an α,β -unsaturated aromatic lactone such as I in lignin has been converted by methanolysis and reaction with diazomethane to the corresponding methoxymethyl ester, II. This has been illustrated as a coumarin type since coumarin has been found to behave in such a manner in a methanolic solution of diazomethane (3); but it is probable that other α,β -unsaturated lactones will act likewise.



Thus according to this formulation an increase in methoxyl content ought to be accompanied by an increase in additivity of Grignard reagent, without involving loss of active hydrogen. Table II shows this qualitatively to be true.

If this effect is indeed due to lactone formation following glycoside hydrolysis during extraction then the acetic formic lignin, which has lost most of its carbohydrate, should show a greater methoxyl increase and a greater Grignard addition than the corresponding acetic lignins after diazomethane-methylation. Table II shows this correspondence.

If this formulation expresses correctly the lignin structure with respect to its carboxyl groups, then methylation with dimethyl sulphate and alkali ought to convert I into the hydroxy acid, III, or the methoxy acid, IV, depending on the acidity of the enolic hydroxyl group.



The results of dimethyl sulphate + alkali-methylation of the various lignin fractions, which are recorded in Table III, tend to support the assumptions. The extent of methylation is, of course, much higher than that attained with diazomethane, since alcoholic and enolic hydroxyls will all be methylated by this reagent. Significantly, however, the lignin still contains free hydroxyl. Its ability to add Grignard reagent has actually decreased from that found

TABLE III
DIMETHYL SULPHATE METHYLATION OF BIRCH LIGNIN

Fraction and solubility	Amount used, gm.	Original OCH_3 , %	Yld., gm.	Final OCH_3 , %	Anal. for		Machine analysis in dioxane	
					C %	H %	Act. H/kgm.	RMgX added /kgm.
Acetic birch								
Ether	1.5	21.0	1.1	34.6	64.6	6.1	1.8	0.9
Benzene	1.8	20.7	1.3	35.0	64.3	6.4	1.7	0.8
Methanol	1.8	18.9	1.4	35.4			1.7	0.8
Chloroform	1.7	16.4	1.3	35.0			1.8	0.7
Acetic-formic birch								
Chloroform	1.2	22.1	1.0	35.8	66.3	6.1	1.6	1.4

for a comparable diazomethane-methylated lignin. This might be expected if ester linkages had been hydrolyzed by the action of the alkali to leave the salts of free carboxyl groups.

Inspection of Table III shows the interesting phenomenon that all fractions have been methylated to about the same OCH_3 content. The carbohydrate originally present in the less soluble fractions has evidently been hydrolyzed during the repeated alkali treatment, because the methoxyl value does not change after treatment with boiling formic acid. But the less soluble fractions originally contained less methoxyl, even on the carbohydrate-free basis. This would indicate that dimethyl sulphate + alkali had converted these less soluble fractions to the chemical equivalent of the more soluble fractions.

These fractions which have been methylated with dimethyl sulphate and alkali are for the most part not completely soluble in aqueous alkali unless much dioxane is added. Indeed they behave as would be expected of a substance of high molecular weight with insufficient hydrophilic groups (such as carboxyl) to effect complete solution. Thus they tend to retain sodium as the salt unless they are strongly acidified.

One of the repeatedly methylated ether + benzene-soluble fractions is, however, completely soluble in the alkaline reaction mixture resulting from treatment with dimethyl sulphate; but after acidification it cannot again be dissolved in the same dilute alkali. A higher concentration over a long period of time is required for solution. It would appear that, in this case, acidification permitted a reversal of the process $\text{I} \rightarrow \text{III}$ and involved re-formation of a lactone.

As might be expected, this fraction (presumably lactonized) increased in methoxyl content from 34.3 to 39.6% when treated with diazomethane, and no decrease was discovered in active hydrogen content. An increase in addition of Grignard reagent was observed which would be expected if I were

converted to II. Further confirmation that diazomethane effected esterification was obtained by saponification with alkali, which reduced the methoxyl content to 33.9%.

The methoxyl content of another, less soluble, fraction (34.0% OCH_3 after dimethyl sulphate-methylation) was increased only to 36.8% by treatment with diazomethane, but the original methoxyl content was restored by alkaline saponification. It may be seen that the differential in methoxyl content is not so great as is the case with the more soluble fractions. This is not unexpected when it is realized that lignin is a complex mixture (not a single compound) and therefore that its chemistry will be qualitatively but not quantitatively exact.

On the basis of these results it is suggested that a carboxyl group with a tendency toward lactonization is present in birch formic or acetic lignin to the extent of less than 1 group per kilogram of lignin.

Experimental

Diazomethane-methylation

The procedure outlined previously (4) was employed, using the diazomethane from 2.5 cc. of nitrosomethylurethane per gram of lignin, in 50 cc. of dioxane. This diazomethane was contaminated with the methanol used in its preparation. Analytical samples of the methylated lignin were prepared by precipitation of dioxane solutions into 10 volumes of petroleum ether (b.p. 40° to 60°). Yields and analyses are shown in Table I.

Dimethyl Sulphate + Alkali-methylation

The method outlined previously (2) was employed with the variation that dioxane instead of acetone was used as the organic solvent. The products, after four treatments with dimethyl sulphate and 30% aqueous sodium hydroxide under nitrogen (reaction distinctly alkaline when reaction complete), were acidified, dissolved in chloroform, and precipitated into petroleum ether (b.p. 40° to 60°). The yields and properties are shown in Table III.

Lactone Nature of More Soluble Fraction

A chloroform solution of 10.5 gm. of dimethyl sulphate+alkali-methylated ether-benzene soluble fraction (OCH_3 , 34.0%) was washed with 1% aqueous sodium hydroxide to remove an alkali-soluble fraction (isolated by acidification of the alkaline extract; wt. 0.78 gm., methoxyl 25.7%). The alkali-insoluble remainder in the chloroform was evaporated to dryness, redissolved in 400 cc. of dioxane, and stirred under nitrogen while 50 cc. of dimethyl sulphate and 150 cc. of 30% aqueous sodium hydroxide were added over an eight hour period. The dioxane layer was separated and poured into 1800 cc. of water to give a clear solution. Upon acidification with hydrochloric acid, a precipitate appeared which was taken up in chloroform. The latter solution, after

evaporation to 150 cc. (20 mm.) was filtered and precipitated into 1500 cc. of petroleum ether (b.p. 40° to 60°). It weighed 7.0 gm., methoxyl 34.3%. It was now again insoluble in 1% aqueous sodium hydroxide. In the Grignard machine, this sample gave 2.2 active hydrogen and 0.6 RMgX added per kgm.; in pyridine it gave 2.7 active hydrogen and 1.6 RMgX added.

Esterification of Dimethyl Sulphate-Methoxylated Ether-benzene Soluble Fraction

A solution of 7.0 gm. (OCH_3 , 34.3%) of this fraction in 280 cc. of dioxane was treated for three days with a diazomethane solution prepared from 10 cc. of nitrosomethylurethane. After vacuum evaporation the lignin was dissolved in benzene and precipitated into 10 volumes of petroleum ether (b.p. 40° to 60°). Weight 5.6 gm.; OCH_3 , 39.6%; Grignard analysis per kgm.: in dioxane 2.4 active H, 1.0 RMgX added; in pyridine, 2.5 active H, 1.1 RMgX added. The centrifuge liquors from this precipitation were evaporated to dryness. The residue in ether was precipitated into petroleum ether (weight, 0.14 gm., OCH_3 , 41.3%).

When 0.4 gm. of the material with 39.6% OCH_3 was dissolved in 25 cc. benzene and boiled 10 hr. with 30 cc. of 5% hydrochloric acid, 0.34 gm. was recovered by precipitation into petroleum ether, OCH_3 , 36.5%.

A 0.3 gm. portion of the material containing 39.6% OCH_3 was allowed to stand two days in a water-dioxane solution of 5% sodium hydroxide. After dilution into water, the precipitate was dissolved in chloroform and reprecipitated into petroleum ether. The 0.25 gm. which was recovered contained sodium and 32.9% OCH_3 . After re-solution in chloroform, it was washed with dilute hydrochloric acid and again precipitated to give a methoxyl value of 33.6% and no sodium.

Dimethyl Sulphate-methylated, Chloroform-methanol Soluble, Fraction

1. Esterification

When 3 gm. of this fraction (OCH_3 , 34.0%) was treated with diazomethane solution for three days, precipitation from benzene into petroleum ether yielded 2.8 gm., methoxyl 36.8%. Grignard analysis in dioxane, per kgm.: 1.5 active H, 1.2 RMgX added.

When this material was saponified by treating a solution in 5 cc. of dioxane with 2 cc. of 5% aqueous sodium hydroxide at 20° C. for 24 hr., the methoxyl content of the acidified reaction product was 34.0% after precipitation from benzene into petroleum ether.

2. Action of Formic or Acetic Acids

One gram portions of this fraction (OCH_3 , 34.0%) were refluxed for 12 hr. with each of these solvents. The product from acetic acid treatment was 1 gm. of material unchanged in methoxyl (34.0%). After treatment with 95% formic acid 0.90 gm. (OCH_3 , 34.4%) was recovered.

Acknowledgment

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THE ISOBUTYL GROUP IN SPRUCE AND BIRCH LIGNINS¹

BY ALAN BELL AND GEORGE F WRIGHT

Abstract

Acetone has been isolated by permanganate oxidation of birch and spruce lignins extracted from wood by acetic or formic acid. Acetone was obtained also when the formic acid lignins were ozonized but not from the acetic acid-extracted lignins. This difference was confirmed when perbenzoic acid titration indicated unsaturation in the formic acid extract which was not present in the acetic acid extract. It is suggested that an α -hydroxy- β -methoxyisobutyl group is present in lignin; during acetic acid extraction the hydroxyl group is acetylated but during formic acid extraction the formic acid reduces the group to isobutenyl, which will give acetone when it is ozonized.

In a brief communication (2) it was announced that acetone had been isolated as an oxidation product of formic acid spruce lignin (9, 11). This oxidation has now been repeated with formic acid spruce as well as with formic acid birch (6) and acetic acid (3) birch lignin. In order to insure that the acetone did not arise from carbohydrate these lignins were first boiled with aqueous 25% *p*-toluenesulphonic acid. The three carbohydrate-free lignins were then oxidized with alkaline potassium permanganate to yield 0.4%, 0.7%, and 0.5% respectively of acetone, determined as the 2,4-dinitrophenylhydrazone.

Thus evidence is at hand that all of these lignins contain the isopropyl group. However, ozonization of these isolated lignins yielded acetone only when the lignins had been isolated from the wood with boiling formic acid (Table I). This extraction agent must therefore react with the lignin to form an isopropylidene radical whereas the acetic acid extraction yields a saturated isopropyl group.

It will be observed (Table I) that less than half of the lignin is destroyed by ozonization, the remainder being recovered as water-soluble and water-insoluble lignin-like products. The former predominate when the ozonization is more complete. From the lignin-like nature of these products it would seem that the essential nucleus is still intact. Only substituent fragments (containing, however, most of the methoxyl content) seem to have been affected by ozone. The remainder, containing about 5% OCH_3 , would appear to have been split at two positions per kilogram of lignin, because the addition of Grignard reagent in pyridine, which is doubled by diazomethane methylation, indicates four carboxyl groups per kilogram of water-soluble ozonization product. This water-soluble product is being investigated in a further study of lignin ozonization.

The presence of an ethylene linkage in formic acid lignins, which was absent in the corresponding acetic acid lignins, was thus demonstrated through

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Contribution from the Chemical Laboratories, McGill University, Montreal, Que., and the University of Toronto, Toronto, Ont.

TABLE
OZONIZATION OF LIGNIN

Before ozonization				After ozonization								
Expt.	Type of lignin	Wt. used, gm.	OCH ₃ in isolated lignin, %	Acetone derivative	Acetone, wt. %	Oxalic acid, wt. %	Water-insoluble		Water-soluble; acetone-ether-insoluble		Water-soluble; acetone-pet. ether-insoluble*	
							Wt., gm.	OCH ₃ , %	Wt., gm.	OCH ₃ , %	Wt., gm.	OCH ₃ , %
1	Methylated acetone-sol., formic birch	10	15.7	0.85 gm. acetone superoxide	6.6		5.0	6.2	2.5			
2	Chloroform-soluble formic birch	10	19.6	0.34 gm. benzalacetone	1.4	4.2			3.3 4.35	5.4 3.7	2.5 0.9	6.1 4.6
3	Chloroform-soluble formic spruce	1	11.7	0.06 gm. acetone superoxide	4.8		0.15					
4	Unfractionated acetic birch	10	17.6	None	None	3.0	0.25		4.5			
5	Methanol-soluble acetic birch	10	14.7	None	None	3.0	0.8		5.7			
6	Unfractionated acetic formic birch, acetylated	10	19.7	None	None	3.1	3.0		1.0			

* Skellysolve F was the petroleum ether used in the precipitations.

ozonization by the preparation of suitable derivatives of acetone. The extent of this unsaturation could not, however, be evaluated by ozonization because of considerable variability in yield. The amount of ethylenic linkage was therefore estimated by perbenzoic acid titration at 0° C. Within two hours the formic acid lignin consumed 0.6 equivalent more of perbenzoic acid than did the acetic acid lignin, and this difference in consumption prevailed during the slow disappearance of the oxidizing agent over 10 days.

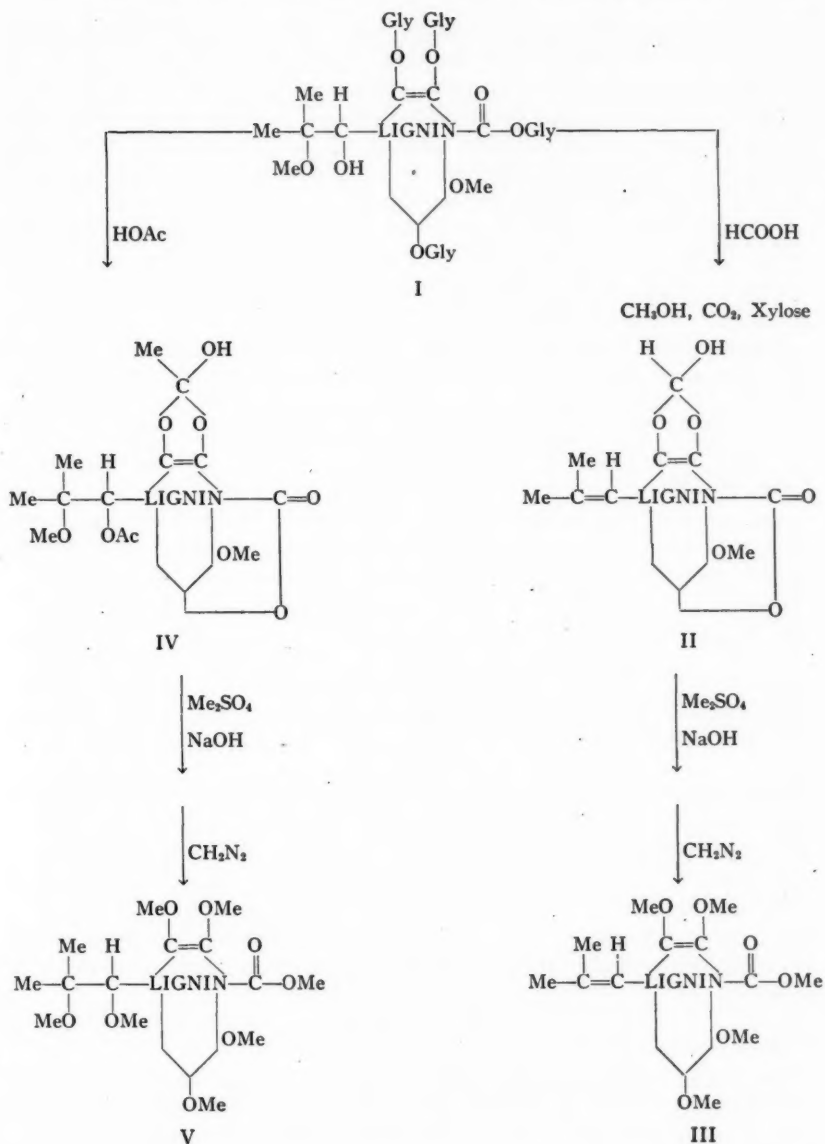
In order to ascertain the mechanism of formation of this additional double bond during the extraction process with formic acid, a comparison of the various birch lignin fractions must be made. Both the benzene-soluble and the benzene-insoluble fractions have been examined for methoxyl, acetyl, or formyl, and for hydroxyl content (Zerewitinoff).

TABLE II
METHOXYL AND ACTIVE HYDROGEN CONTENTS OF ACETIC, FORMIC, AND ACETIC-FORMIC LIGNINS

Type and fraction of lignin	Methoxyl groups per kgm., ester and carbohydrate-free basis	Hydroxyl groups per kgm. (Grignard active H in pyridine)	Ester content		Total free esterified hydroxyl groups per kgm.
			Acetyl groups per kgm.	Formyl groups per kgm.	
Acetic					
Benzene-sol.*	7.6	8.4	0		8.4
Benzene-insol.	6.3	7.9	0.5		8.4
Formic					
Benzene-sol.	7.0	5.7		1.1	6.8
Benzene-insol.	5.7	6.7		0.8	7.5
Acetic formic					
Benzene-sol.	7.7	6.1	1.2		7.3
Benzene-insol.	6.2	7.7	1.1		8.8

* This lignin had been saponified with sodium hydroxide.

Data in Table II compiled from previous studies of these acetic (3) and formic (6) lignins show that, as compared with acetic acid extract, the formic birch lignins have lost both methoxyl groups and active hydrogen during the extraction from wood. However, when the acetic acid extract is *subsequently* treated with boiling formic acid, no methoxyl loss and very little loss in active hydrogen (hydroxyl groups) is noted. This would indicate that treatment with acetic acid has blocked groups with which the formic acid could otherwise react. On the basis of acetate-ester content, such blocked groups should have been hydroxyl. This evidence may be interpreted by a formulation which depicts the known characteristics of acetic and formic birch lignins.



This formulation represents lignin in wood as I, with phenolic, ene-diolic, and carboxylic (3, 4) hydroxyls presumably bound to the wood polysaccharide glycosidically. The extraction with formic acid to give formic acid birch lignin, II, has previously been assumed not only to break the glycosidic linkages

but also to form a 2-hydroxy-1,3-dioxole ring. This hemi-orthoester formation at the ene-diolic linkage is postulated to account for the introduction of two methoxyl groups by diazomethane treatment of a saponified formic acid lignin where only one hydroxyl group was indicated by Grignard analysis before saponification. It has also been assumed (3) that the carboxyl group when freed from its glycosidic bonding forms a coumarin-type of lactone (8). Finally the present research indicates a 1-hydroxy-2-methoxyisobutyl radical in natural lignin, I, which is converted by formic acid into the isobutenyl group shown in II. This ethene formation is remindful of the conversion of glycerol to allyl alcohol (10) and may also involve an orthoformate intermediate (7). Eventual methylation of II will then give III.

Extraction of wood by acetic acid, on the other hand, will give the acetic birch lignin, IV, containing the 1-acetoxy-2-methoxyisobutyl group; the lateral methoxyl is retained and the lateral hydroxyl group in I is acetylated because acetic, unlike formic acid, would not convert a 1,2-glycol to an ethene. Eventual methylation of IV will thus give V, somewhat richer in methoxyl than III.

According to this concept, formic acid birch lignin II differs from acetic acid birch lignin IV by containing 0.6 double bond instead of 0.6 methoxyl and 0.6 acetoxy group per kgm. of lignin. A corresponding difference of 1.2 methoxyl group per kgm. should then appear when these lignins are completely methylated with respect to dimethyl sulphate and diazomethane. Actually, the difference in the completely methylated lignins between the acetic fraction A (OCH_3 , 39.6%) and the formic fraction A (OCH_3 , 34.8%) is approximately the same as between the acetic fraction B (OCH_3 , 36.6%), (V), and the formic fraction B (OCH_3 , 32.3%), (III), namely 1.4 to 1.5 methoxyl groups per kgm. It is evident therefore from the methoxyl values that the acetic acid lignin has more hydroxyl function available for methylation than has the formic acid lignin, although the difference is greater (by 0.3 group per kgm.) than was expected from the perbenzoic titrations. This discrepancy may be owing to the titration (ozonolysis gave a higher acetone value, but it is difficult to dry acetone superoxide). However, it is more likely to be owing to incomplete recovery from the methylation of a nonhomogeneous material such as lignin, and from faults arising in the methoxyl determination of lignins (1).

Experimental

Ozonization of Lignins

The solvent, chloroform, was washed with concentrated sulphuric acid, then with 10% potassium hydroxide, dried with calcium chloride, then treated with ozone for several hours, finally washed with dilute hydrochloric acid followed by continuous water washing for 12 hr. One hundred cubic centimeters of the dried, distilled solvent was used per gram of lignin. In case the lignin was not chloroform-soluble, either methylation (Table I, Expt. 1) or acetylation (Expt. 6) conferred on the lignin the requisite solubility. The solution was chilled with an iced water bath, and dry oxygen containing 12%

ozone was passed through until analysis of the effluent gases showed that no more ozone was being absorbed.

The resulting solution, bleached from a dark red to a turbid light yellow color, was evaporated at 35° to 40° C. (15 mm.), leaving a yellowish-white residue. If the latter was treated with 26 cc. of 1% hydrogen peroxide for 12 hr., followed by 30 min. reflux, acetone superoxide was obtained on steam distillation. If water rather than hydrogen peroxide were used for this treatment, acetone was isolated as an aqueous distillate (water being added during the distillation). The acetone in this aqueous distillate was isolated either as the 2,4-dinitrophenylhydrazone (m.p. 125° to 128° C.), or as dibenzalacetone (m.p. 108° C.) by treating the alkaline solution with an excess of benzaldehyde. Mixed melting points served to identify both substances. In the recorded experiment (Table I, No. 2) the benzalacetone isolated required an excess of acetone; the yield is therefore not significant.

The water-insoluble lignin material (sodium bicarbonate-soluble) was filtered off. The amount of this varied inversely with the completeness of ozonization and contained 6 to 8% methoxyl. Upon diazomethane methylation of the material (Table I, Expt. 1), this methoxyl was increased to 21.2%; Grignard analysis, 4.2 active H and 1.9 RMgX added per kgm. in dioxane.

The solution from which the water-insoluble material was filtered was now extracted continuously with ether for three days. When the ozonized material had been treated with hydrogen peroxide, the residue obtained by evaporation of the ether yielded acetone superoxide upon sublimation at 40° to 50° C. (10 mm.). After sublimation at this temperature was complete, an increase to 100° to 120° C. (10 mm.) yielded oxalic acid. Both substances were identified by mixed melting point with authentic samples.

The aqueous solution, following continuous ether extraction, was evaporated to dryness at 15 mm. (much foaming). The residue was dissolved in acetone and precipitated into ether to yield water-soluble lignin-like material containing 3.5 to 5.5% methoxyl. The ethereal centrifuge liquors contained a lignin-like material which was difficult to reprecipitate into petroleum ether (Skellysolve F) because of contamination with oxalic acid.

A weight of 4.35 gm. of this water-soluble lignin was obtained (Table I, Expt. 2). In the Grignard machine in dioxane this material gave 4.5 active H and 0.6 RMgX added per kgm.; in pyridine 9.3 active H and 4.4 RMgX added per kgm. After two treatments with diazomethane, the methoxyl value was increased to 20.6%; Grignard analysis in dioxane, 3.5 active H and 1.4 RMgX added per kgm.; in pyridine 9.2 active H and 9.7 RMgX added per kgm.

Oxidation of Lignins with Alkaline Permanganate

The lignin was first freed from carbohydrate by boiling with aqueous *p*-toluenesulphonic acid. In a typical experiment, 8.5 gm. of acetone-soluble spruce lignin (9) (OCH₃, 12.7%; HCO, 3.5%) was heated to 100° C. with 500 cc. of 25% *p*-toluenesulphonic acid for four hours. The hydrolyzed mixture was then distilled at 15 mm. from a Claisen flask totally immersed in

a water bath, the side arm being filled with glass wool. When the water bath temperature reached 100° C. and the residue was completely dry, 200 cc. of water was added and the distillation process repeated. The distillate was neutralized with alkali and redistilled to remove 0.07% formaldehyde, determined as the dimedone derivative. The residual sodium salts gave strong tests for formate (5) but no trace of acetate could be detected by treatment of the sodium salt with *p*-nitrobenzyl chloride.

The de-formylated lignin was a black mass which was still soluble in dilute sodium hydroxide. It was washed until neutral to Congo red paper to eliminate *p*-toluenesulphonic acid; incidentally, soluble carbohydrate should also be removed by this treatment. The washed lignin was dissolved in 520 cc. of 0.4% sodium hydroxide and stirred at room temperature while 67 gm. of potassium permanganate was added over a three-day period. The flask was then fitted with an antifoaming device and stirred while 200 cc. was distilled over. This aqueous distillate was boiled 10 min. with 0.5 gm. of 2,4-dinitrophenylhydrazine, concentrated hydrochloric acid being added through the reflux condenser. After cooling, the solution was extracted four times with acetone-free chloroform. The latter solution was evaporated to dryness and freed from unchanged 2,4-dinitrophenylhydrazine by extraction with a *minimum* quantity of chloroform. Evaporation of this chloroform solution left 0.15 gm. of acetone 2,4-dinitrophenylhydrazone, m.p. 122° C., purified by crystallization from ethanol-dilute hydrochloric acid, m.p. 126° to 127° C., not lowered by mixed melting point. This corresponds to a 0.4% weight yield of acetone.

The residual oxidation product was treated with sulphur dioxide to dissolve manganese dioxide. The acidified solution was continuously extracted with ether; the residue upon evaporation of the ether extract was sublimed at 120° C. (10 mm.) to give a sublimate from which, by extraction with benzene, 0.01 gm. of succinic anhydride, m.p. 115° to 116° C., was obtained and identified by mixed melting point of the resublimed product, m.p. 118.5° C., with an authentic sample. The benzene-insoluble sublimate was soluble in acetone; it sublimed at 240° C. (760 mm.) and melted above 270° C.

An identical procedure with unfractionated acetic birch lignin (OCH₃, 17.0%) yielded 0.18% formaldehyde and 0.5% acetone. Formic birch lignin (acetone-soluble, OCH₃, 21%) under similar conditions for oxidation gave 0.7% acetone.

Perbenzoic Acid Oxidation of Lignins

One gram of chloroform-soluble formic birch lignin (OCH₃, 20.1%) dissolved in chloroform was cooled to 0° C. and diluted to a definite volume with a cold solution of perbenzoic acid (0.065 mole per liter) in chloroform. The reaction was maintained at 0° C., while 1 cc. portions were withdrawn at intervals and transferred to 20 cc. of water in a 100 cc. distilling flask. The chloroform in the aliquot was removed by evaporation under 20 mm. at room temperature and the residual solution treated with 2 cc. of 5% potassium

iodide and 3 cc. of 12% hydrochloric acid and titrated slowly and with difficulty using *N*/100 sodium thiosulphate and 10 to 15 drops of 0.2% starch solution.

This procedure was repeated with ether-soluble acetic birch lignin (OCH_3 , 19.2%). Comparison of the titration values shows that the formic acid lignin rapidly consumed 0.6 equivalent of perbenzoic acid per kgm. more than the acetic acid lignin, after which the rates of perbenzoic acid disappearance were equal over 10 days at 0°C .

TABLE III

TITRATION OF LIGNIN - PERBENZOIC ACID SYSTEM, ML. *N*/100 THIOSULPHATE
Reaction time, min.

Lignin type	0	400	4000	8000	16,000
Formic acid	6.50	5.82	4.63	4.09	3.25
Acetic acid	6.50	6.10	4.93	4.38	3.58

When the titration of aliquots indicated that the reaction was complete, the solutions, which were much lighter in color following the treatment with perbenzoic acid, were washed with 10% sodium thiosulphate followed by sodium hydroxide solution. Following a subsequent wash with 1% hydrochloric acid, the chloroform layer was evaporated at 20 mm. pressure. The residue was fractionated according to solubilities in benzene, chloroform, or dioxane. Because of the light color of the solution, the optical rotation was measured for a number of these samples; found $[\alpha]_{589}^{26}$, -3° to -5° in chloroform.

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THE ULTRAVIOLET ABSORPTION SPECTRA OF NITRIC ACID SOLUTIONS¹

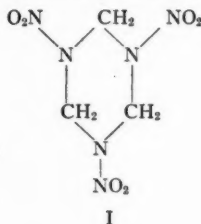
BY R. NORMAN JONES AND G. DENIS THORN

Abstract

The ultraviolet absorption spectra of binary mixtures of nitric acid, water, acetic acid, acetic anhydride, and nitrogen pentoxide have been investigated over the ranges of concentration in which the systems exhibit sufficient chemical stability. The variations in the spectra are considered in relation to the other physical properties of the systems, as reported in the literature. The ultraviolet spectrum of nitric acid in the presence both of nitrogen pentoxide and water is interpreted in terms of a series of equilibria which involve the nitrate (NO_3^-) and nitronium (NO_2^+) ions and associated and nonassociated neutral molecules. The specific gravities of anhydrous nitric acid solutions of ammonium nitrate, potassium nitrate, ammonium acetate, acetic acid at $20 \pm 0.1^\circ \text{C}$. and of nitrogen pentoxide at $25 \pm 0.1^\circ \text{C}$. are also reported.

Introduction

The explosive 1,3,5-trinitro-1,3,5-triazacyclohexane (I), commonly known as RDX, is manufactured by two processes. In the "Direct" process, hexamine (hexamethylenetetramine) is nitrated with a large excess of nitric



acid of 97.5 to 99.5% concentration by weight. In the "Combination" or "Bachmann" process a solution of hexamine in glacial acetic acid is mixed simultaneously with acetic anhydride and with a solution of ammonium nitrate in nitric acid. Considerable research has been carried out on the mechanisms of these nitration reactions. In the case of the Combination process there are reasons to believe that the reaction is one of considerable complexity, and the yields of RDX are highly sensitive to small variations in the conditions of the reaction and the composition of the reaction mixture. In the simpler Direct process the yields also vary considerably with the strength of the nitric acid.

In an attempt to gain information about the mechanism of nitration of hexamine under the conditions operative both in the Direct and Combination

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processes, an investigation has been made of the ultraviolet absorption spectra of the individual reagents concerned in these processes, and of such binary mixtures of these reagents as are sufficiently stable at room temperature to allow of their spectrographic measurement.

The systems investigated are summarized in Table I, and are considered separately in the succeeding sections of the paper. There follows a general

TABLE I
SYSTEMS EXAMINED

System	Concentration*
A. Ammonium nitrate - water	0-80% ammonium nitrate
B. Nitric acid - water	0-20% water
C. Nitric acid - ammonium nitrate	0-54% ammonium nitrate
D. Nitric acid - potassium nitrate	0-25% potassium nitrate
E. Nitric acid - ammonium acetate	0-30% ammonium acetate
F. Nitric acid - acetic acid	0-80% acetic acid
G. Nitrogen pentoxide - acetic acid	0.054 molar with respect to nitrogen pentoxide
H. Nitrogen pentoxide - acetic anhydride	4.79 molar with respect to nitrogen pentoxide
I. Nitrogen pentoxide - carbon tetrachloride	0.282 and 0.102 molar with respect to nitrogen pentoxide
J. Nitric acid - nitrogen pentoxide	0-24% nitrogen pentoxide
K. Nitric acid - acetic anhydride	0-12 and 94-100% acetic anhydride

* Per cent composition by weight unless otherwise indicated.

discussion, and a section devoted to a description of the experimental techniques which were developed for the measurement of the spectra of thin films of highly corrosive materials. The general conclusions have been presented in a preliminary report (31).

A. Ammonium Nitrate - Water

Although no record of the ultraviolet absorption spectrum of aqueous solutions of ammonium nitrate has been found in the literature, the absorption is similar to that of solutions of the nitrates of the alkali metals. Hartley (25, 26) in 1902 measured the absorption spectra of aqueous solutions of several metallic nitrate salts, and observed a broad band in the region of 3020 Å; the position and intensity of this band varied only slightly with change in the cation, and he attributed it to the nitrate ion. In 1909, Baly, Burke, and Marsden (1) determined the spectra of alcoholic solutions of various nitrates and of nitric acid, and confirmed Hartley's observation that the band near 3020 Å is caused by the nitrate ion. Schaefer (41, 42) in 1915 observed that alkyl nitrate esters, unlike the nitrate salts, did not exhibit the 3020 Å absorption band; their spectra showed only "end absorption" with

no maxima detectable in the measured region of the spectrum (compare Fig. 1). Scheibe (44), Hantzsch (22) and von Halban and Eisenbrand (16, 17, 19) have measured the absorption spectra of sodium and potassium nitrates in the presence of various salt solutions, and have noted that the

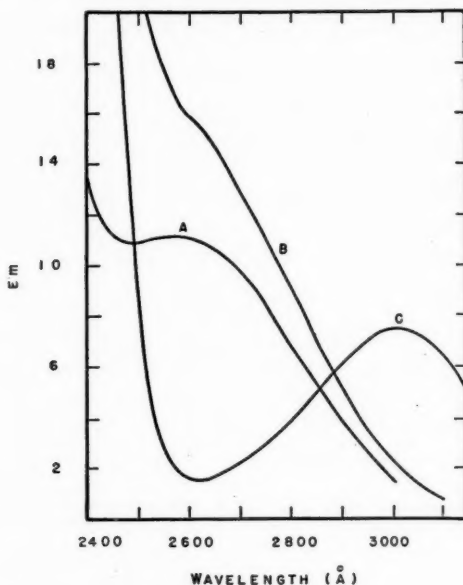


FIG. 1. Ultraviolet absorption spectra.

Curve A. Anhydrous nitric acid.

Curve B. Ethyl nitrate.

Curve C. Aqueous solution of ammonium nitrate.

molar extinction coefficient of the nitrate ion maximum at 3020 Å falls in intensity with increase in the concentration of the secondary electrolyte, while a new maximum appears at shorter wave lengths. Hantzsch (22) attributed these changes to solvation effects.

Experimental Observations

In these laboratories the absorption spectra of aqueous solutions containing from 0.99 to 805.4 gm. of ammonium nitrate per liter of solution have been measured. Over this concentration range the position of the maximum remains constant at 3015 Å (Fig. 1. Curve C); the molecular extinction coefficient at the maximum ($E_{m_{max}}$) changes only slightly, falling from 7.6 for dilute solutions to 6.9 for the most concentrated solution (see Table II). This absorption maximum can, without doubt, be attributed to the nitrate ion, and it may be inferred from the data in Table II that aqueous solutions of ammonium nitrate undergo little change in ionic condition as the concentration increases.

TABLE II

ABSORPTION OF AQUEOUS AMMONIUM NITRATE. INTENSITY AT THE MAXIMUM

Concentration, gm./liter	$\log \frac{I_0}{I}$	Depth of solution, mm.	E_m at 3015 Å
0.99	0.094	10.00	7.5
2.99	0.279		7.5
3.32	0.316		7.6
4.67	0.433		7.4
5.53	0.517		7.5
10.83	0.107	1.06	7.4
20.01	0.196		7.5
30.30	0.306		7.6
40.07	0.397		7.5
	0.043	0.114	7.5
100.81	0.116		7.4
150.2	0.156		7.3
250.9	0.251		7.0
276.1	0.275		7.0
330.9	0.330	0.0196	6.9
396.7	0.395		7.0
517.1	0.524		7.1
	0.090		7.1
805.4	0.136		6.9

B. Nitric Acid - Water

The ultraviolet absorption spectrum of nitric acid has received extensive study from several investigators. The spectra of dilute solutions of nitric acid are similar to those of the alkali nitrates (1, 17, 18, 19, 22, 26, 33, 37, 41) but changes occur as the concentration of the nitric acid is increased. Hartley (26) noted that the nitrate ion absorption band near 3020 Å disappeared with increase in the nitric acid concentration. Schaefer (41-43) measured the absorption of aqueous solutions containing up to 98.6% of nitric acid by weight, and found no maxima for concentrations greater than 63% (14 N): his data indicate that 92% acid (22 N) exhibits a higher intensity near 2600 Å than 99% acid (23.7 N) (*vide infra*). The absorption of 0.2 N potassium nitrate dissolved in sulphuric acid of increasing concentration was similar to that of increasing concentrations of nitric acid in water. Von Halban and Eisenbrand (19) investigated the absorption of nitric acid at concentrations up to 68% (15.3 N) and noted the decrease in the intensity of the nitrate ion band with increasing concentration. They also observed a maximum at 2650 Å in the spectrum of solutions of nitric acid in anhydrous ether and attributed this band to the presence of unionized HO-NO₂ molecules. Hantzsch (21, 22) found no maximum in the absorption curve of 100% nitric acid, nor in the curve of a solution of nitric acid in anhydrous ether; he did note that a band appeared on addition of a trace of water to such an ethereal solution. Hantzsch discusses both his own work and that of Von Halban and Eisenbrand in a long critical paper (22) in which he explains the effects of dilution on the spectrum of nitric acid in terms of a complex series of equilibria involving a hydrolysis of "nitracidium nitrate" $\{[ON(OH)_2]^+ NO_3^-\}$

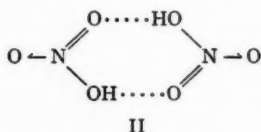
to a "pseudoacid" ($\text{O}_2\text{N}-\text{OH}$) followed by hydration of the pseudo acid and, on further addition of water, its conversion to "hydroxonium nitrate" $[(\text{NO}_3)\text{H}_3\text{O}]$ which then ionizes.

Although, as will be apparent later, the changes which occur on the increasing addition of water to anhydrous nitric acid must involve a series of equilibria comparable in complexity with those postulated by Hantzsch, most of this earlier spectrometric work would seem to be reconcilable with a simple ionic equilibrium between unionized nitric acid molecules ($\text{HO}-\text{NO}_2$) with an absorption maximum at 2600 to 2650 Å and a nitrate ion with a weaker absorption maximum at 3015 to 3020 Å, viz.,



Except for some measurements by Dalmon and Bellin (11, 12) and by Kortüm (33), little work appears to have been done recently on the ultraviolet absorption of concentrated solutions of nitric acid, but it is relevant to consider some measurements on other physical properties. The *refractive indices* of aqueous solutions of nitric acid when plotted against the per cent composition give a linear relation over the range from 78 to 91%. At 91% a sharp inflection occurs, and above 98.5% the slope of the line is reversed (48). The *electrical conductivity* also behaves abnormally over this concentration range, as was observed by Veley and Manley (48) and confirmed recently in these laboratories by Taylor (31).

Several investigators have examined the *infrared* and *Raman spectra* of aqueous solutions of nitric acid. Dalmon and Freyman (13) have recorded the very near infrared spectrum of 80 to 100% nitric acid, and have noted an absorption band at 1.017μ in the spectrum of the anhydrous acid, which they attributed to the associated molecule II. On the progressive addition of water this band diminishes in intensity and a new band develops at 0.97μ .



At a concentration of 80% the 1.017μ band has almost disappeared. Dalmon and Freyman consider that the 0.97μ band may be due to a hydroxyl group. These observations confirm earlier work of Kinsey and Ellis (32). A theoretical treatment of the infrared absorption spectrum of nitric acid has recently been attempted by Bauer and Magat (2), the results of which are claimed to be in accordance with the observations of Dalmon and Freyman.

Nitric acid below 30% gives a *Raman spectrum* similar to that of the alkali nitrates and differing from the spectrum of the concentrated acid (3, 7-9, 15, 35, 36, 38-40, 45).

When the concentration is increased above 30% new Raman lines appear. In the spectrum of the anhydrous acid no lines attributable to the nitrate ion

are observed; two faint lines ($\Delta \nu$ 1050 cm^{-1} and 1400 cm^{-1}) in the spectrum of anhydrous nitric acid were attributed by Chédin to nitrogen pentoxide, which he estimates may be present in anhydrous nitric acid to the extent of about 1%. Chédin observed that these weak bands can still be seen in acid of 99.6% concentration. Most of the studies on the Raman spectrum of nitric acid have been qualitative only, and no systematic studies over the range from 80 to 100% at small increments in concentration appear to have been made. This subject has been reviewed by Hibben (28).

Recently Bennett, Brand, and Williams (4, 5) have put forward evidence indicating that solutions of nitric acid in sulphuric acid may contain molecular species other than HONO_2 and NO_3^- , and they attribute the Raman line at 1400 cm^{-1} to the nitronium (NO_2^+) ion.

These abnormalities in the physical constants of concentrated nitric acid solutions are of particular interest in relation to the marked influence of acid concentration on the yields of RDX obtained in the nitration of hexamine. They suggest that some species of molecule or ion may be present in maximal concentration in nitric acid containing a small but significant amount of water, a molecule or ion which may be the primary agent in the nitration process.

Experimental Observations

The ultraviolet absorption spectra of aqueous solutions of nitric acid have been determined over the concentration range from 80 to 100% nitric acid. A maximum occurs at 2565 Å in the spectrum of the anhydrous acid with $E_{m_{\max}}$ 11.1. The position of the maximum shifts to 2615 Å as the concentration falls to 95% and remains unchanged with further dilution to 90%. With diminishing concentration the molecular extinction coefficient at the maximum decreases to 9.5 for 95% acid, increases again to 11.5 for an acid of 92% strength, and then falls slowly on further dilution. These changes are shown in the series of curves in Fig. 2. In Fig. 3 the value of $E_{m_{\max}}$ is plotted against the acid concentration. In Table III the wave lengths and the intensities at the maxima are listed for all the nitric acid samples studied. The value of $E_{m_{\max}}$ in the last column is an averaged value of two or more spectrographic measurements on the same acid sample. The reproducibility of $E_{m_{\max}}$ on a series of determinations on the same sample of diluted acid was about 2%. However, the values obtained for $E_{m_{\max}}$ on different preparations of acid diluted to approximately the same concentration varied in some cases by several per cent. These variations are responsible for the scatter of the points in Fig. 3. They are caused most probably by uncertainties in the determination of the acid concentration (see Experimental Section, page 602).

C. Nitric Acid - Ammonium Nitrate

It does not seem that the ultraviolet absorption spectrum of ammonium nitrate dissolved in anhydrous nitric acid has been determined previously, but Médard and Petitpas (35, 36) have examined the Raman spectra of such

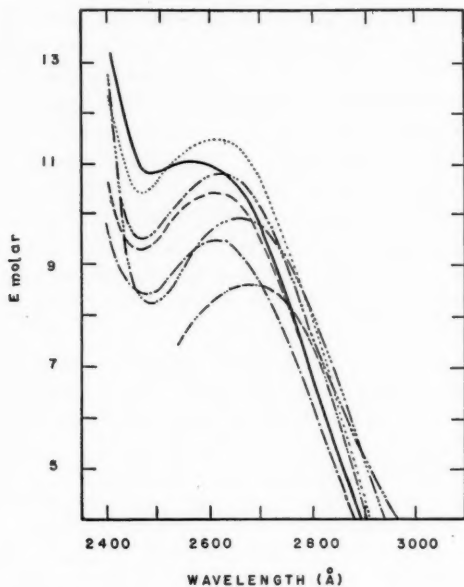


FIG. 2. Ultraviolet absorption spectra of aqueous nitric acid:—

————	100.0% HNO_3	-----	90.0% HNO_3
-----	97.0%	80.1%
- · - · -	95.0%	-----	68.6%*
.....	92.2%		

(*) Taken from data of von Halban and Eisenbrand (reference 19).

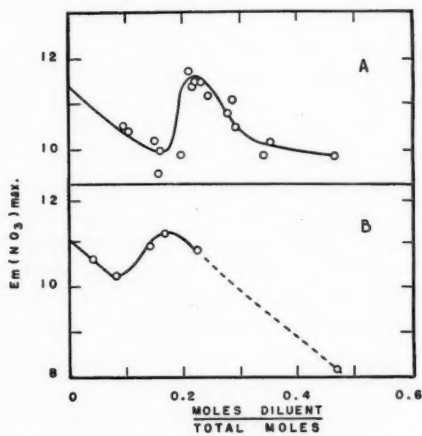


FIG. 3. Variation of the molecular extinction coefficient at the maximum for nitric acid.
A. Dilution with water; B. Dilution with ammonium nitrate.

TABLE III
 ABSORPTION SPECTRUM OF 80 TO 100% NITRIC ACID. POSITION
 AND INTENSITY OF THE MAXIMUM

Concentration		Wave length of maximum, Å	E_{max} (individual measurements on the same acid sample)	E_{max} (average)
% Nitric acid	Mole fraction of water			
100.0	0.000	2565	11.15, 11.30 11.10, 11.01 10.90	11.1
97.2	0.092	2600	10.40, 10.40, 10.80	10.5
96.9	0.101	2610	10.70, 10.55, 10.15	10.4
95.3	0.147	2610	10.40, 10.52, 9.90, 10.20	10.2
95.0	0.155	2610	9.54, 9.54	9.5
94.9	0.158	2610	9.92, 10.02	10.0
93.6	0.193	2615	9.84, 9.93	9.9
93.0	0.208	2610	11.68, 11.80	11.7
92.7	0.213	2615	11.43, 11.43	11.4
92.6	0.218	2610	11.80, 11.40, 11.40	11.5
92.2	0.228	2610	11.50, 11.48	11.5
91.7	0.240	2615	11.20	11.2
90.1	0.277	2615	10.80, 10.82	10.8
89.9	0.282	2615	11.10, 11.10	11.1
89.5	0.291	2625	10.60, 10.35	10.5
87.2	0.339	2635	9.90, 9.95	9.9
83.4	0.409	2650	10.30, 10.30, 10.15	10.2
80.1	0.465	2650	9.88, 10.00	9.9

solutions. They note that, on the addition of the salt, shifts occur in the positions of the Raman lines similar to those produced by the addition of small amounts of water.

Experimental Observations

The ultraviolet absorption spectra have been measured of solutions containing up to 54 gm. of ammonium nitrate in 100 gm. of solution.* The results are recorded in Table IV and in Fig. 4.

The effect of addition of ammonium nitrate on the ultraviolet absorption spectrum of anhydrous nitric acid parallels the effects noted by Médard on the Raman spectrum. Small additions cause a fall in the intensity of the absorption maximum near 2625 Å. Further addition of ammonium nitrate causes the intensity of E_{max} to increase and at higher concentrations it again falls. These variations are plotted against the concentration in Fig. 3. The considerable shift of the wave length of the absorption maximum in the mixture containing 54% ammonium nitrate is probably caused in part by the additive effect of the nitrate ion absorption maximum at 3015 Å contributed by the anion of the added salt.

* At the temperature at which these spectra were measured (approximately 20° C.) a two phase system occurs for nitric acid-ammonium nitrate mixtures over the concentration range between 27 and 52% of ammonium nitrate by weight. A single phase is obtained between 52 and 57% and below 27% ammonium nitrate.

TABLE IV
ABSORPTION SPECTRUM OF NITRIC ACID - AMMONIUM NITRATE. POSITION
AND INTENSITY OF THE MAXIMUM

Concentration		Wave length of maximum, Å	$E_{max} (NO_3)^*$
% NH_4NO_3	Mole fraction NH_4NO_3		
0.0	0.000	2565	11.1
5.0	0.040	2615	10.6
10.0	0.080	2625	10.3
17.0	0.139	2635	10.9
20.0	0.165	2650	11.2
26.8	0.224	2665	10.8
54.0	0.470	2775	8.2

* See page 598.

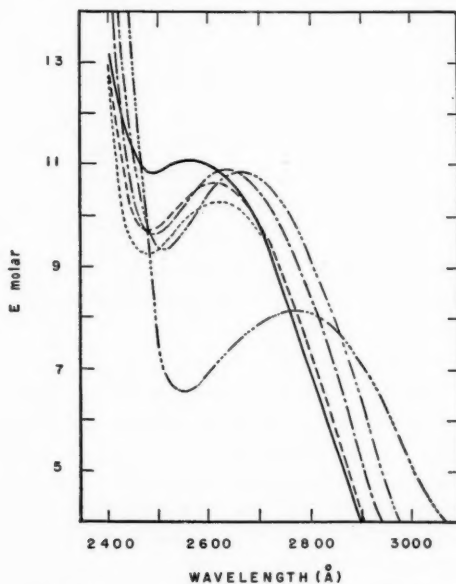


FIG. 4. Ultraviolet absorption spectra of nitric acid - ammonium nitrate mixtures.

—————	100.0% HNO_3	-----	17.0% NH_4NO_3
- - - - -	5.0% NH_4NO_3	-----	26.8% "
.....	10.0% "	-----	54.0% "

D. Nitric Acid - Potassium Nitrate

Experimental Observations

The ultraviolet absorption spectra of solutions containing up to 25% of potassium nitrate in anhydrous nitric acid are shown in Fig. 5, and the

variation of E_{\max} is plotted in terms of the mole fraction of potassium nitrate in Curve A of Fig. 8.

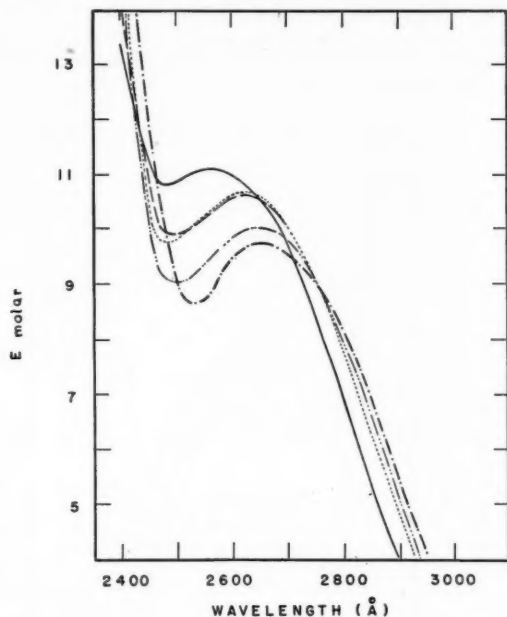


FIG. 5. Ultraviolet absorption spectra of nitric acid - potassium nitrate mixtures.

—————	100.0% HNO_3	- - - - -	20.0% KNO_3
- - - - -	10.0% KNO_3	— · — · —	25.0% KNO_3
·····	15.0% KNO_3		

There is a suggestion that E_{\max} does not diminish steadily, and an inflexion may be present in the neighborhood of 0.1 mole potassium nitrate. A similarity to the behavior of the nitric acid-ammonium nitrate system is indicated but the data are insufficient to establish this with certainty.

E. Nitric Acid - Ammonium Acetate

Experimental Observations

The spectra of solutions containing up to 30% of ammonium acetate in anhydrous nitric acid are recorded in Fig. 6. As with the other binary systems of salts with nitric acid, there is a suggestion of a fall and subsequent rise to a maximum in the curve of E_{\max} plotted against increasing concentration of the added salt (Fig. 8).

During the manipulation of these solutions the odor of acetic acid seemed to increase as the concentration of the ammonium acetate became larger.

In order to determine whether acetic acid was being produced in accordance with the equilibrium:



a ternary solution of ammonium nitrate, nitric acid, and glacial acetic acid was prepared; the molecular proportions of the three constituents were

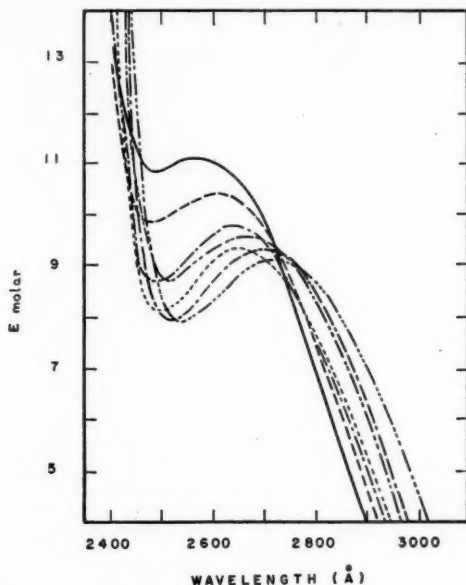


FIG. 6. Ultraviolet absorption spectra of nitric acid-ammonium acetate mixtures.

—————	100.0% HNO_3	- - - - -	20.6% NH_4OAc .
- - - - -	5.0% NH_4OAc .	- - - - -	25.0% "
- · - · - ·	9.8% "	- · - · - ·	29.9% "
·····	15.0% "		

adjusted to yield the same molar proportions* as in the most concentrated of the ammonium acetate-nitric acid solutions shown in Fig. 6. Both the densities and the absorption spectra of these two solutions were the same. Taylor (46) has investigated the electrical conductivity of mixtures of nitric acid, acetic acid, and ammonium acetate, and has observed that solutions of identical conductivity can be prepared by mixing either ammonium acetate and nitric acid or ammonium nitrate and acetic acid in suitable proportions.

*For the curve indicated as —·—·—·—·—· the mole fraction of ammonium acetate was 0.259. This ternary solution was made up to have a mole fraction of acetic acid of 0.258, ammonium nitrate 0.258, and nitric acid 0.484. The molecular extinction coefficient at the maximum calculated for nitric acid was 9.0, and can be compared with 9.1 for the ammonium acetate-nitric acid solution.

F. Nitric Acid - Acetic Acid

Viscosity and freezing point measurements suggest that compound formation may occur between these two acids, but the Raman spectra of such mixtures exhibit the characteristic frequencies of each component without the appearance of any new lines (6).

Experimental Observations

The ultraviolet absorption spectra of solutions containing up to 50% of anhydrous acetic acid in anhydrous nitric acid are shown in Fig. 7. When

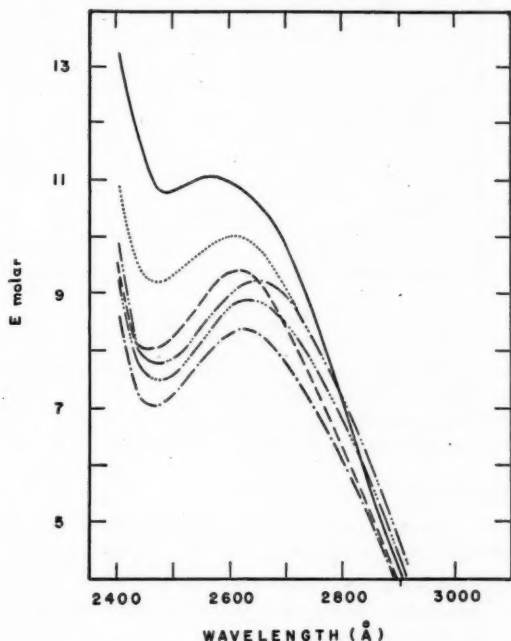


FIG. 7. Ultraviolet absorption spectra of nitric acid - acetic acid mixtures.

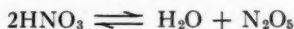
—————	100.0% HNO_3	-----	30.6% HOAc.
.....	7.0% HOAc.	-----	39.0% "
-----	12.3% "	-----	49.4% "

the intensity at the maximum is plotted against the composition of the solution, the same type of curve is obtained as with the other binary systems containing nitric acid (Fig. 8).

G, H, I. Nitrogen Pentoxide

The changes in the absorption spectrum of anhydrous nitric acid brought about by the addition of small quantities of water or other solutes might arise

from the effects of the solute on an equilibrium, in "anhydrous nitric acid," between nitric acid, water, and nitrogen pentoxide, viz.:—



This consideration prompted the extension of these investigations to include systems containing nitrogen pentoxide.

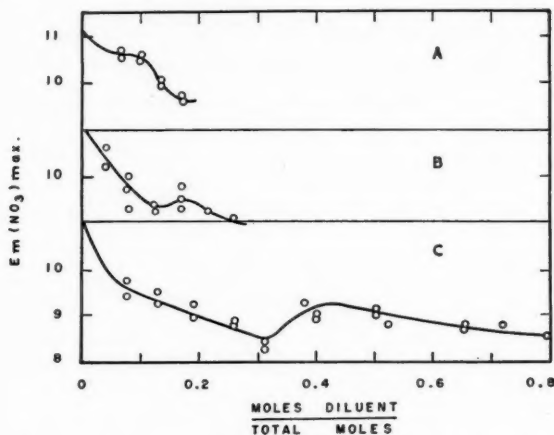


FIG. 8. Variation of the molecular extinction coefficient at the maximum for nitric acid.

- A. Dilution with potassium nitrate.
- B. Dilution with ammonium acetate.
- C. Dilution with acetic acid.

Experimental Observations

The spectra of nitrogen pentoxide in acetic acid, acetic anhydride, and in carbon tetrachloride are recorded in Fig. 9. These show no maxima, but indicate that the absorption is very intense below 2700 Å. In acetic acid the spectrum differs somewhat from that in the other solvents, there being evidence of an inflection at 2750 Å.

J. Nitric Acid – Nitrogen Pentoxide

Experimental Observations

The spectra of solutions of anhydrous nitric acid containing up to 24% by weight of nitrogen pentoxide are recorded in Fig. 10. It is seen that as the amount of nitrogen pentoxide is increased, the absorption maximum at 2615 Å soon becomes obliterated by the intense absorption of the added solute.

K. Nitric Acid – Acetic Anhydride

Experimental Observations

The range of concentration over which this system can be investigated is limited, since, at room temperature, mixtures containing from 12 to 94% of

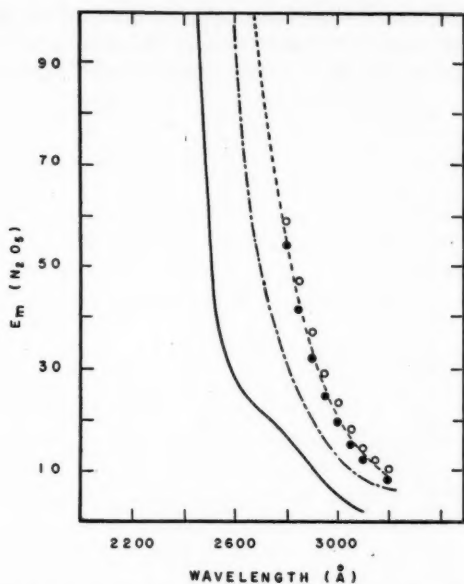


FIG. 9. Ultraviolet absorption spectrum of nitrogen pentoxide in various solvents.

————— 0.054 molar solution in acetic acid.
 4.79 molar solution in acetic anhydride.
 - - - - - ●●● 0.282 molar solution in carbon tetrachloride.
 " ○○○ 0.102 molar solution in carbon tetrachloride.

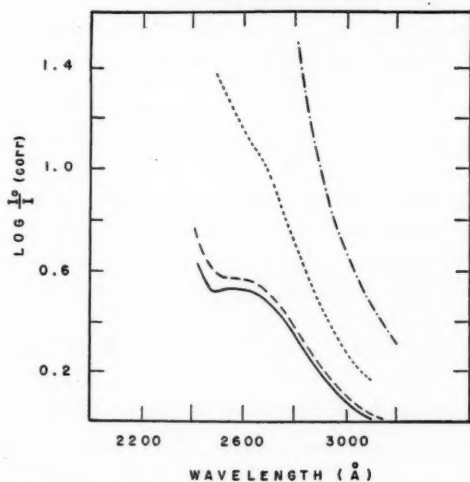


FIG. 10. Ultraviolet absorption spectra of nitric acid - nitrogen pentoxide mixtures (optical density corrected for change in the specific gravity of the solution. See page 598).

————— 100% HNO₃
 - - - - - 3% N₂O₅
 12% N₂O₅
 - · - · - 24% N₂O₅
 (Cell thickness 0.0196 mm.)

acetic anhydride are unstable and are liable to undergo spontaneous decomposition. The spectra of mixtures outside of this unstable range which were examined are shown in Fig. 11. These curves exhibit significant similarities

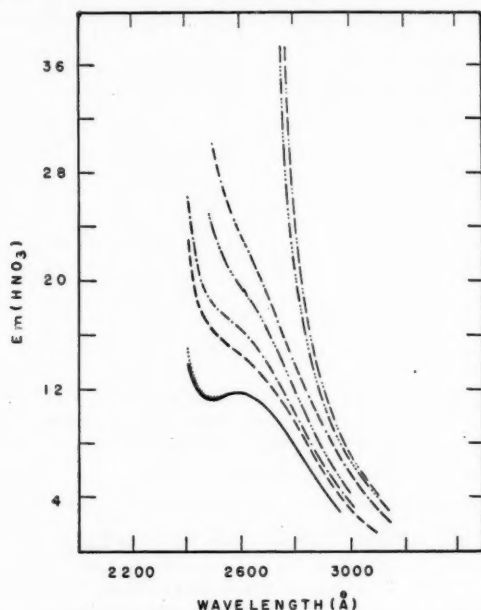


FIG. 11. Ultraviolet absorption spectra of nitric acid-acetic anhydride mixtures.

—————	1.26% Ac_2O	-----	12.16% Ac_2O
.....	3.19% "	-----	94.72% "
- - - - -	6.74% "	-----	96.84% "
-----	7.24% "		
.....	9.46% "		

to the curves for the nitric acid-nitrogen pentoxide system shown in Fig. 10. At high concentrations of acetic anhydride the curves resemble those of high concentrations of nitrogen pentoxide in nitric acid, and at low concentrations of acetic anhydride they resemble the solutions of low concentrations of nitrogen pentoxide in nitric acid. Since acetic anhydride is nonabsorbent in this region of the spectrum (24, 34), these observations suggest the existence of an equilibrium:—



in which the equilibrium position lies well to the right-hand side.

Discussion

A comparison of the absorption spectra of nitric acid solutions containing small amounts of water (Fig. 2) with the spectra of nitric acid solutions

containing small amounts of nitrogen pentoxide (Fig. 10) suggests that the latter group of curves manifest a continuation of a series of changes which commences with the 95% acid and passes smoothly through the anhydrous acid to the acids containing excess nitrogen pentoxide.*

With this in mind, the changes in the spectra of aqueous nitric acid which occur over the concentration range from 80 to 100% may be described in the following terms. Between 80 and 95% a molecular species predominates which is responsible for the absorption maximum near 2600 Å. This molecule or ion, which may be designated the "2600 Å chromogen" is present in maximal concentration at 91 to 92%. At 95 to 96%, changes occur in the spectrum which can be attributed to the presence of "free nitrogen pentoxide" in the solution.

In Table V the *persistence* of the 2600 Å band is listed for various concentrations; the persistence is defined as the ratio of the molecular extinction coefficient at the maximum near 2600 Å to that at the minimum near 2500 Å. The persistence constitutes a convenient numerical index of the prominence of the absorption band, and its continuous diminution with increasing nitric acid concentration indicates that the curve is progressively flattening. This effect is superimposed on the rise of E_{2600} to a maximum at 91 to 92%.

It would seem necessary to invoke two variables to explain these changes, (a) an increase in the concentration of the 2600 Å chromogen between 80 and 92% and (b) the appearance of a new molecular or ionic species exhibiting intense structureless absorption, which we have tentatively identified above as "free nitrogen pentoxide."

Examination of the persistence values in Table V shows furthermore that between 97 and 100% the rate of fall is greater than at lower nitric acid concentrations, indicating that small decreases in water content produce progressively greater increases in the "free nitrogen pentoxide" concentration as the anhydrous condition is approached.†

Between 93 and 96% the absolute intensity of the maximum falls off. In view of the very great intensity of the nitrogen pentoxide absorption, the concentrations of this substance required to produce the observed flattening

* Hantzsch (22) has questioned the claim of von Halban and Eisenbrand (19) that an ethereal solution of anhydrous nitric acid possesses an absorption maximum at 2650 Å; he reported that no such maximum is present if the ether is truly anhydrous, a maximum appearing only on the addition of a drop of water to the solution. Hantzsch also failed to observe any maximum in the absorption spectrum of anhydrous nitric acid. One would infer from Hantzsch's paper that the maximum observed by von Halban and Eisenbrand resulted from the use of moist ether. Hantzsch's failure to detect the maximum in the spectrum of nitric acid, either in the free state or in ethereal solution, might very well be caused by his using anhydrous nitric acid containing appreciable quantities of dissolved nitrogen pentoxide.

† One of the referees has commented on our use of the persistence concept and has suggested that we try to use the E values to calculate the percentage of nitrogen pentoxide present at various concentrations. This had been considered previously, but the idea was discarded since the molecule or ion actually contributing to the absorption which we attribute to "free nitrogen pentoxide" is almost certainly a constituent of an equilibrium mixture and its absorption is very unlikely to obey a Beer's law relation based on the nitrogen pentoxide curves in Fig. 9. A strict mathematical treatment of the curves seemed of doubtful significance in these circumstances. We therefore used the persistence treatment so as to be able to describe the changes of curve shape with concentration in a semiquantitative manner.

TABLE V
PERSISTENCE OF THE 2600 Å BAND IN NITRIC ACID - WATER

% HNO ₃	E_{max}/E_{min}	% HNO ₃	E_{max}/E_{min}
100	1.02	90	1.14
97	1.12	87	1.17
95	1.13	80	1.20

effect must be exceedingly small, and it would seem reasonable to surmise that in addition to the formation of free nitrogen pentoxide, other factors may be operative over this concentration range in reducing the concentration of the 2600 chromogen.

The nature of the 2600 chromogen has been discussed by earlier workers, and von Halban and Eisenbrand (19) identify it with the nonassociated HO-NO₂ molecule (Hantzsch's pseudoacid). This would seem to be largely a speculative hypothesis, although it is supported to some extent by the resemblance to the spectrum of the alkyl nitrate esters (Fig. 1). The effect of the addition of small amounts of water, acetic acid, or various inorganic salts in bringing about an increase in the concentration of this species is difficult to explain. If the existence of associated molecules which are non-absorbent in this region of the spectrum be postulated, the observed effects could be explained by assuming that the added solute brings about a "deassociation". This would be in line with Dalmon and Freyman's interpretation of the changes in the infrared spectrum of nitric acid on dilution with water to 80% (see page 584).

It is relevant to note here that the system nitric acid - ammonium nitrate exhibits no unusual features over the measured concentration range which would suggest specific complex formation or other abnormal type of behavior to account for its essential role in the Bachman process for the manufacture of RDX.

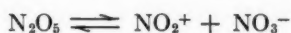
Nitrogen Pentoxide

The main source of information concerning the presence of nitrogen pentoxide in nitric acid is the Raman spectrum (28). It has already been noted (page 584) that in the Raman spectrum of anhydrous nitric acid a line appears at $\Delta\nu = 1400\text{ cm}^{-1}$. This line is very prominent in anhydrous nitric acid containing 20% of phosphorus pentoxide, as also are two lines 1050 and 1100 cm^{-1} , which are faint in the spectrum of pure anhydrous nitric acid. In the Raman spectrum of crystalline nitrogen pentoxide there are two lines at 1050 and 1400 cm^{-1} which are identical in position with those which augment in intensity on addition of nitrogen pentoxide to anhydrous nitric acid. The same lines occur also in the Raman spectra of certain nitric acid - sulphuric acid mixtures (4, 5, 9).

These lines are not seen in the spectra of solutions of nitrogen pentoxide in carbon tetrachloride or phosphorus oxychloride, there being instead three other prominent lines near 1330, 1250, and 880 cm^{-1} . The infrared spectrum of gaseous nitrogen pentoxide is very similar to that of a solution in carbon tetrachloride (10, 27). The evidence from Raman and infrared spectra thus indicates that nitrogen pentoxide exists in one form in the gaseous state and in solution in chlorinated solvents, and in a different form in the crystalline state and in solution in anhydrous nitric acid.

Bennett, Brand, and Williams (4, 5) have drawn attention to these anomalies in the Raman spectrum of anhydrous nitric acid, and in support of their contention that the Raman line at 1400 cm^{-1} in mixtures of nitric acid - sulphuric acid is caused by the NO_2^+ ion they make use of the ingenious argument that such an ion would be isosteric with carbon dioxide and might be expected to possess similar vibrational characteristics. Carbon dioxide possesses a prominent Raman line near 1400 cm^{-1} . It would seem to us that this hypothesis necessitates the further conclusion that, as a line is present also at the same frequency in the Raman spectrum of nitrogen pentoxide in the crystalline state, that too contains the NO_2^+ ion, suggesting an ionic lattice structure of NO_2^+ and NO_3^- ions. If this is so, some evidence of the presence of NO_3^- might be expected to show up in the infrared spectrum of crystalline nitrogen pentoxide.*

Up to 1946 no real evidence of the presence of NO_2^+ or other nitrogen containing cation in nitric acid (in the absence of sulphuric acid) had been obtained, except possibly for Hantzsch and Berger's observation (23) that, on the electrolysis of "nitracidium perchlorate" in nitromethane solution there occurs a migration of nitrogen containing groups toward the cathode. In these laboratories Taylor, Lyne, and Follows have investigated the electrical conductivity of the system water - nitric acid - nitrogen pentoxide and shown that the equivalent conductivity is minimal for 96% acid, increases sharply as the acid approaches the anhydrous condition, and continues to increase smoothly as nitrogen pentoxide is added. This would indicate an increase in the ionic population of the solution above 96%. To explain this, Taylor suggested that nitrogen pentoxide may be undergoing ionic dissociation as shown below; such dissociation need not be extensive to explain the observed conductivity changes.



The ultraviolet absorption spectra of the water - nitric acid - nitrogen pentoxide system are readily reconcilable with this hypothesis. In such a system the weak absorption of the nitrate ion at 3020 Å may be obliterated by more intense "nitrogen pentoxide absorption". The latter might be caused by the NO_2^+ ion, or by the undissociated nitrogen pentoxide molecule.

* A similar hypothesis concerning the structure of crystalline nitrogen pentoxide has been advanced by Ingold, Millen, and Poole (30).

coefficients from these measurements it was necessary to know the molar concentration, which involved the determination of the specific gravities of the solutions. Such measurements of specific gravity have been carried out on the following systems:—

Nitric acid – ammonium nitrate

Nitric acid – potassium nitrate

Nitric acid – ammonium acetate

Nitric acid – acetic acid.

The results are given in Table VI and in Fig. 12.

TABLE VI
DENSITIES OF ANHYDROUS NITRIC ACID SOLUTIONS

% NH_4NO_3	D_4^{20}	% KNO_3	D_4^{20}	% NH_4OAc	D_4^{20}	% HOAc	D_4^{20}	% N_2O_5	D_4^{25} *
0.00	1.513	—	—	—	—	—	—	0.0	1.501
5.01	1.527	9.98	1.582	5.02	1.508	12.70	1.441	6.0	1.530
10.81	1.548	14.97	1.621	9.84	1.501	28.40	1.361	12.0	1.560
19.72	1.568	19.99	1.658	14.95	1.491	37.17	1.322	18.0	1.588
26.75	1.579	25.00	1.695	20.60	1.478	49.40	1.265	24.0	1.618
54.00	1.578	—	—	25.00	1.459	66.37	1.186	30.0	1.645
—	—	—	—	29.90	1.440	79.70	1.131	—	—

* Data supplied by Dr. E. G. Taylor

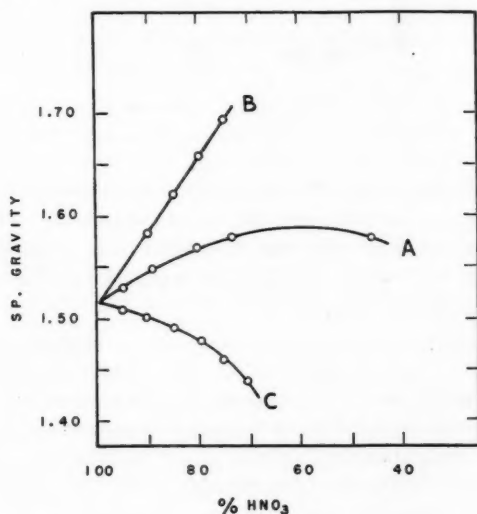


FIG. 12. Specific gravities (d_4^{20}).

A. Nitric acid – ammonium nitrate.

B. Nitric acid – potassium nitrate.

C. Nitric acid – ammonium acetate.

The values for the specific gravity of aqueous solutions of nitric acid were taken from the International Critical Tables, and for solutions of nitrogen pentoxide in nitric acid from measurements made by Dr. Taylor in this laboratory. Approximate values for nitrogen pentoxide in acetic anhydride and in carbon tetrachloride were obtained by interpolation between the specific gravity values of solid nitrogen pentoxide (2.0), acetic anhydride (1.08), and carbon tetrachloride (1.59), assuming a linear variation with concentration. The data in Table VI represent the mean of duplicate determinations based on comparison of the weight of 10 ml. of solution with 10 ml. of water, using a volumetric flask as a pyknometer. Measurements were made at $20.0 \pm 0.1^\circ \text{C}$., and a correction for buoyancy applied. The precision in most cases is better than 0.001, and in no case was a variation greater than 0.002 observed.

Spectrographic Manipulation

A Beckman model DU ultraviolet spectrophotometer was used for the determination of the spectra. The majority of the solutions possessed too great an optical density to permit use of the standard 1 cm. cells. Cells were designed as shown in Fig. 13. They consisted of optically plane quartz disks

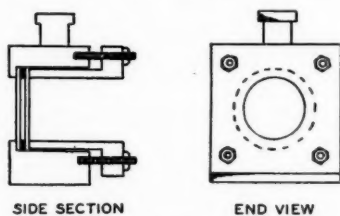


FIG. 13. Thin cell for corrosive solutions.

separated by platinum annuli and held in place in an aluminum holder. The quartz disks were 1 mm. thick and 26 mm. in diameter. The annuli were stamped from platinum sheet of 0.012, 0.1, and 1 mm. thickness. Aluminum and platinum were used as the metals most suitable to withstand the action of concentrated nitric acid (47).

A specially designed compartment containing a sliding carriage to hold two of these cells was placed between the main case of the spectrograph and the photocell compartment. Two quartz windows permitted entrance and exit of the monochromatic light beam through this compartment, and provision was made for the aspiration of a stream of air through the compartment to remove any corrosive fumes from the neighborhood of the spectrophotometer.

The cells were calibrated photometrically using potassium chromate (20, 29). The potassium chromate was recrystallized four times from 0.005 *N* potassium hydroxide and dried by pumping at 10^{-5} mm. for five hours. Several determinations of the optical density of standard chromate solutions

were made for each cell. Using the value of E_{max} given by Hogness *et al.* (29) the cell thickness (l) was calculated from Equation (1).*

Two methods were employed in filling these cells. In the first method, which could be employed only for nonhygroscopic and nonvolatile material, the annulus and one quartz disk were placed on the inner section of the aluminum holder. A few drops of the liquid were then placed on the quartz disk. The second quartz disk was then lowered on to the annulus, after which the outer section of the holder was slipped over the inner section and tightened (Fig. 14a).

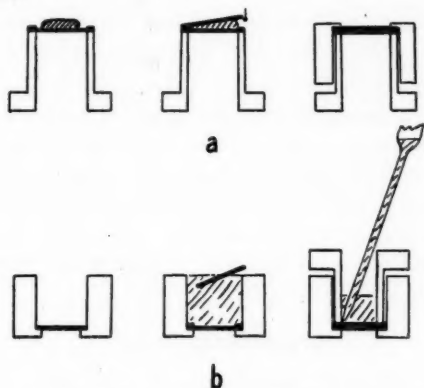


FIG. 14. Diagrammatic illustration of technique for filling thin cell.

- a. For nonhygroscopic solutions.
b. For hygroscopic solutions.

The second method was used for hygroscopic acids. The outer section of the aluminum holder was placed in a shallow crystallizing dish, and one quartz disk lowered into place. The cavity of the cell holder was filled with the acid solution and the annulus and second quartz disk then slid into the solution and pushed down into place with a glass rod. The inner section of the holder was inserted, the excess acid removed with a pipette, and the whole tightened. Using this method of filling, the portion of solution which is confined between the quartz disks is never exposed to the air in a thin film (see Fig. 14b).

Reagents and Materials

Ammonium nitrate and ammonium acetate—Merck Reagent grade.

Potassium nitrate—"Analar" Reagent.

The ammonium nitrate and potassium nitrate were found to contain less than 0.1% moisture and were therefore used without further treatment.

* In these calculations it is assumed that Beer's law holds accurately for solutions of potassium chromate over the concentrations used. The validity of this assumption is demonstrated by the agreement in the values of the molecular extinction coefficients for ammonium nitrate solutions (Table II) obtained with the same solution in cells of different thickness, since these cell thicknesses are based on measurements of the potassium chromate solutions as described above.

The ammonium acetate was pumped at 1 mm. pressure for several hours and used directly after pumping.

The nitric acid was prepared in an all-glass still. A mixture of two parts by volume of 96% sulphuric acid and one part of 70% nitric acid was distilled at a pressure of 30 mm. of mercury at 60° to 70°. A water-white product was obtained of 99.5 to 100.5% nitric acid content, which gave no test for chloride or sulphate ion. Solutions of lower concentration were prepared by diluting 40 or 50 gm. of the anhydrous acid with the calculated weight of water. The final concentration was determined by titrating a diluted sample with 0.2 *N* sodium hydroxide using phenolphthalein as indicator.

The acetic acid, acetic anhydride, and nitric acid - nitrogen pentoxide mixtures were prepared by Dr. E. G. Taylor and Dr. A. G. Follows in connection with investigations of electric conductivity carried out simultaneously with these spectrographic measurements. The acetic acid was obtained by careful fractionation of Reagent grade glacial acetic acid, the purity being checked by freezing point determinations. The acetic anhydride was distilled from calcium carbide and then fractionally redistilled. Nitrogen pentoxide was prepared by distillation of equal parts by weight of phosphorus pentoxide and anhydrous nitric acid at reduced pressure.

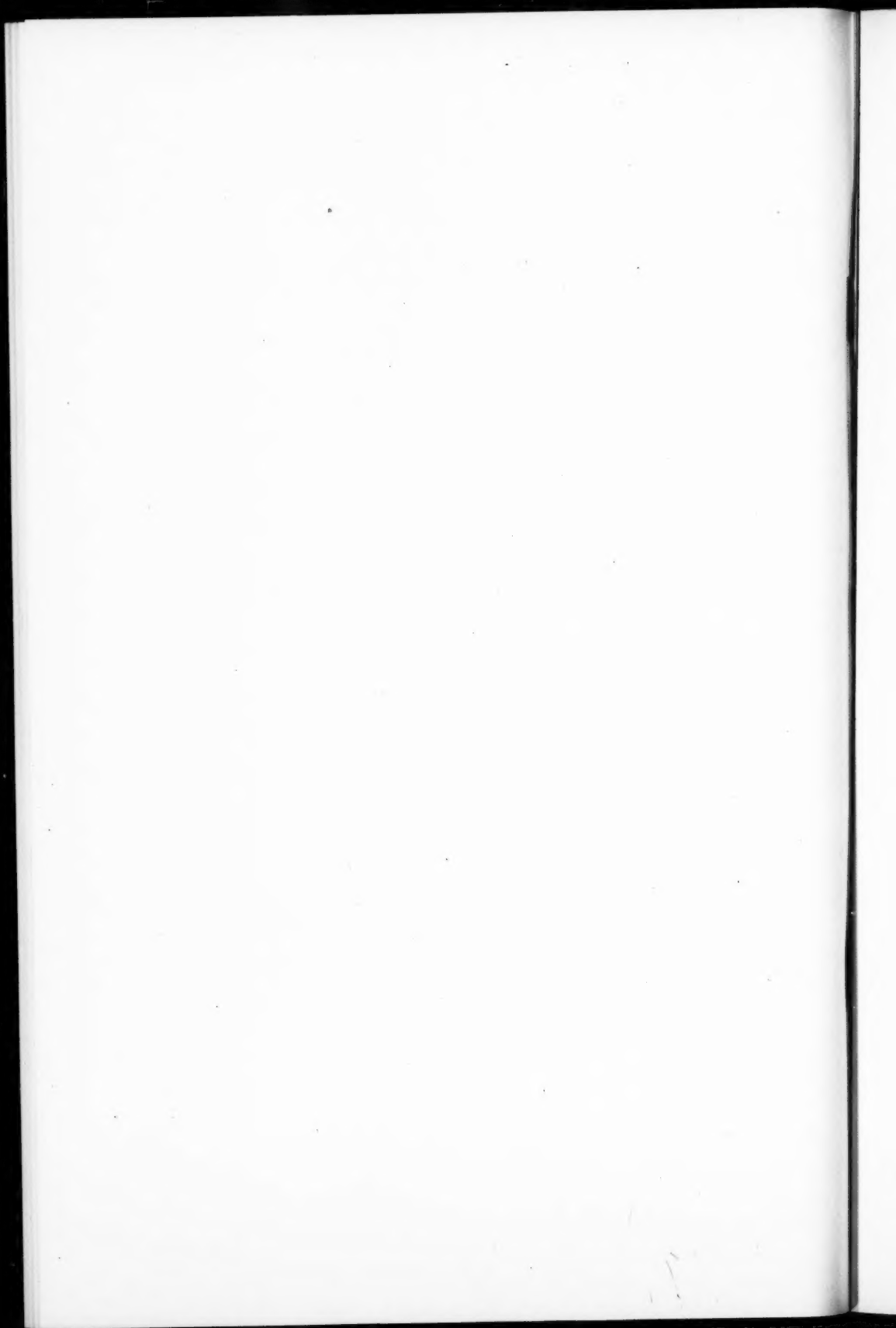
Acknowledgments

During the course of these investigations we had many fruitful discussions with Dr. E. G. Taylor, whose studies of the electrical conductivities and phase diagrams of certain of these systems will be published separately. Our thanks are also due to Dr. A. G. Follows and Mr. M. Lyne for supplies of anhydrous nitric acid and nitrogen pentoxide.

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